ChemEd

EDITORIALLY SPEAKING

The Changing Role of the Science Teacher

Within the last few years our knowledge of science has grown so explosively that the science teacher is faced with problems and responsibilities which teachers of earlier generations could not even imagine. If he is to fill this new role, the teacher must constantly expand his knowledge of science and must greatly improve his methods of teaching. It is an exciting challenge, but a difficult one.

It has been calculated from the number of articles appearing in the scientific literature that more than half of all of the chemical research which has ever been published has appeared within the lifetime of the average college student. Not only have new elements, new compounds, and new processes been discovered, but our concepts of the nature of matter have been almost remade. The vocabulary of the chemistry student today abounds with phrases which express ideas which did not even exist a few years ago—atomic fusion, Lewis acid, π-electron, carbonium ion, molecular orbital, radiocarbon dating, chelation, cyclotron, and many more. Some of this great store of knowledge is of academic interest only, but we are surrounded by evidence that a great deal of it has found application in thousands of ways. Paradoxically, however, these developments have not been paralleled by an increasing interest in science on the part of the general public. Americans, at least in the past, have been quite willing to accept the bounties of science without making any attempt to understand them, or to appreciate the men or the methods that have made them possible. Indeed, anti-intellectualism and contempt for learning have been almost characteristic of our time.

With the successful launching of the Russian satellite Sputnik, an abrupt change took place in the attitude of the American public toward science. Chemists and physicists—indeed, scholars of almost every kind—achieved a new status in the eyes of the public, and teachers of science came to be looked upon with a new respect. After three decades of struggling against a waning interest in science, we must now struggle equally hard to meet the new demands for more rigorous and better teaching, both at the high school and college levels. The new role, while it is more flattering than the old, is much more difficult, for it requires a better knowledge of science and better teaching methods, as well as the exercise of leadership and keen imagination. The chemistry student of today must learn much more than did his predecessors of a generation ago, for there is a great deal more to learn; in order to prevent giving him an impossible load, the teacher must continually revise his course, including new material which is of real significance, and culling out older topics which are outmoded or of diminishing importance. This is a task of unending and increasing difficulty, and many teachers neglect it, either by failing to include newly discovered facts and new theories, or by teaching only the new material with no regard for the way in which the current concepts developed. Of these two faults, the latter is

(*Continued on page 156*)

JOHN C. BAILAR, JR., 1959 President of the American Chemical Society, is well known to readers of these pages. He has served the Division of Chemical Education as chairman and THIS JOURNAL as a member of the Editorial Board. He is "Mr. Inorganic Chemistry" to many, including the inorganic chemists themselves who elected him the first chairman of their newly formed Division in 1957. As an author he has ranged from "Essentials of College Chemistry" to the monumental ACS monograph "The Chemistry of Coordination Compounds" and as an Editor-in-Chief of "Inorganic Syntheses." The University of Illinois where he is now head of the Division of Inorganic Chemistry has been, since 1928, the base from which his travels in behalf of chemistry and professional chemists have taken him to all parts of the world. Few chemists are better qualified to state the case for "The Changing Role of the Science Teacher."

A ChemEd SYMPOSIUM

Instruction in Polymer Chemistry

The symposium,[1] jointly sponsored by the Polymer Division and the Division of Chemical Education, was organized to bring before a larger audience some of the current problems encountered in the teaching of polymer chemistry. Because the study of polymers has only recently received recognition as a separate branch of chemistry, all too frequently this entire area is never touched upon in the undergraduate chemistry curriculum. As a result, the majority of our beginning graduate students have no previous acquaintance with polymer chemistry, and no appreciation of the broad scope of fascinating research problems which it offers. On the other hand, due to the very rapid growth in the commercial importance of polymers, a substantial proportion of today's graduating chemists are finding employment in the polymer industry. It appears certain that the demand of industry for chemists with some polymer training will continue to increase in the foreseeable future.

This situation creates a problem which is essentially twofold: first, how to bring polymer chemistry to the attention of larger numbers of undergraduate students, and second, the type of graduate curriculum which will best enable our students to make a maximum contribution to the research in this new field.

There was general agreement on the immediate need for a pioneering effort to incorporate the elementary principles of polymer chemistry into the courses which traditionally form the basis for the undergraduate program. The first part of the symposium, the papers by Ferry, Mayo, and Price, gave abundant specific examples of the way in which this can be accomplished.

The second portion of the symposium concerned the teaching of polymer chemistry, either in industry or at the graduate level. As pointed out in the paper by Kice, more than half of the institutions granting degrees in chemistry have no polymer chemist on their staffs. This means that graduate level courses in polymer chemistry must be taught in these schools by men of other research interest. Any means of attracting more academic chemists to do research with macromolecules should help alleviate this situation.

The remaining papers provided a cross-sectional view of the methods in use today to teach polymer chemistry at the graduate level. The essential problem is how to introduce the necessary polymer chemistry into the curriculum (which in many cases is already overcrowded) without diluting the student's basic knowledge in the four traditional areas of chemistry on the one hand, or seriously infringing upon his research time on the other. In addition to those printed here, a paper was read by C. K. Bump, J. D. Cotman, Jr., and E. H. Merz of Monsanto on their experience in teaching polymer chemistry in industry. C. G. Overberger of Brooklyn Polytechnic Institute told of the organization and course offerings of their "Polymer Division" in the Chemistry Department. Maurice Morton described the graduate program in polymer chemistry at the University of Akron, where the majority of the doctoral level work at the institution is in the polymer field.

The solutions presented show a remarkable lack of uniformity, the course offerings ranging from a single survey course designed to acquaint all graduate chemistry students with some of the fundamental principles, to a complete program (including both lecture and laboratory courses) which covers in detail both basic principles and the practical applications of polymers. Only the test of experience will reveal which of these alternatives best satisfies the requirements of this growing field.

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[1] A symposium sponsored jointly by the Division of Polymer Chemistry and the Division of Chemical Education at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

The Changing Role—Continued

probably the more serious, for a student who does not learn that each generation builds its theories on those of the previous generation will fail to realize that the ideas which he is taught must surely give way to better ones in a few years; thus, he will have failed entirely to catch the spirit of scientific inquiry.

With the rapid growth of our knowledge of science, however, no teacher can trim enough from his courses to include all of the material that should be included in it; he must, therefore, develop more efficient methods of teaching, both by improving his own presentation of the subject matter and by using TV, demonstrations, moving pictures, and the many other teaching aids which are now available to him.

Though the role which the teacher plays varies with the growth of our chemical thinking and with the tenor of the times, his fundamental task never changes—to encourage and inspire his students, and to give them a vision of what *can* be. He must never forget that "the mind is a pyre to be kindled, not a vessel to be filled."

JOHN C. BAILAR, JR.

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Contributions of Vinyl Polymerization to Organic Chemistry

One of the most important segments of industrial chemistry in both research and production is polymer chemistry. With a relatively high probability of future employment in some phase of polymer work, chemistry students require knowledge of this field as part of their education. The object of this paper is not to belabor that rather obvious point, but to stress that even chemists who never will work in polymerization need some exposure to this field to appreciate an important portion of organic chemistry. For understanding the reactions of free radicals in solutions, vinyl polymerization provides the most and the best data. These free radical reactions include much of organic chemistry which is not associated with polymerization, most of the reactions of carbon-hydrogen bonds in aliphatic compounds and in aromatic side-chains; more specifically, most oxidations with oxygen, most halogenations, and most degradations (by oxygen, heat, or radiation). Polymerization data also shed light on reactions of organic ions.

There are only three important reactions of atoms and free radicals. I shall illustrate all of them with polymerization data. To present these reactions in suitable perspective, all the conventional steps in the polymerization of styrene are summarized in Table 1.

Table 1. Polymerization of Styrene by Free Radicals

Initiator $\xrightarrow{\text{(heat or light)}}$ 2 radicals ($R\cdot$)

(1a) $R\cdot + H_2C{=}CH\phi \rightarrow R{-}CH_2{-}CH\phi\cdot$

(1b) $R{-}(CH_2{-}CH\phi)_n\cdot + H_2C{=}CH\phi \rightarrow R{-}(CH_2{-}CH\phi)_{n+1}\cdot$

(2) $R{-}(CH_2{-}CH\phi)_n\cdot + CCl_4 \rightarrow R{-}(CH_2{-}CH\phi)_n{-}Cl + Cl_3C\cdot$

(1c) $Cl_3C\cdot + H_2C{=}CH\phi \rightarrow Cl_3C{-}CH_2{-}CH\phi\cdot$

(3) $R{-}(CH_2{-}CH\phi)_n\cdot + R{-}(CH_2{-}CH\phi)_{m+1}\cdot \rightarrow$
$R{-}(CH_2{-}CH\phi)_n{-}(CH\phi{-}CH_2)_{m+1}{-}R$ (coupling) or
$R{-}(CH_2{-}CH\phi)_n{\cdot}H + R{-}(CH_2{-}CH\phi)_m{-}CH_2{=}CH\phi$ (disproportionation)

The first general reaction of free radicals is *addition to a double or triple bond.* Although reactions (1*a*) and (1*c*) also exemplify addition, we shall be concerned with (1*b*), the process which produces essentially all the polymer. By using mixtures of styrene with other monomers and by determining compositions of copolymers produced, the relative reactivities of many monomers with many kinds of polymer radicals have been determined.

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The second general reaction of radicals is *abstraction of a univalent atom* from another molecule. Reaction (2) shows the reaction of a "styrene radical" (radical with a free valence on a terminal styrene unit) with carbon tetrachloride, but hydrogen atoms as well as halogen atoms are commonly transferred. This reaction is known as "radical displacement" with small molecules; in reaction (2), a styrene radical has displaced a trichloromethyl radical from a chlorine atom. In polymerization, reaction (2) is called "chain transfer"; the activity (free valence) of one molecule has been transferred to another molecule.

The third general reaction of free radicals is *reaction with other radicals.* Although atoms may react only by coupling, radicals with β-hydrogen atoms (reaction 3), may react either by coupling or by disproportionation.

Two other reactions of radicals are less important and are not discussed here: re-arrangement and cleavage, the latter corresponding to the reverse of reaction (1).

The methods employed to gather the data of this paper assume that the reactivity of a polymer radical depends essentially on the free valence associated with the terminal monomer unit. With rather few exceptions (*1*), the reactivity of the terminal radical is independent of the number or kinds of other units in the polymer radical.

Polymerization studies show that reactivity in free radical reactions depends upon two independent factors. The first factor (previously known qualitatively) is resonance stabilization of reaction species. The more a reacting radical is stabilized by resonance, the less reactive it is and vice versa. Also, the more the radical to be formed from a substrate is stabilized by resonance, the easier the substrate reacts. This is because the transition state involves contributions from both the initial and final states. Therefore, the more resonance stabilization appearing in the product radical, the more this resonance will contribute to the transition state and the lower will be the activation energy. Thus, triphenylmethane is much more reactive than methane toward atoms and radicals.

The second factor governing free radical reactions is the polar effect, which was discovered in copolymerization. This polar effect has been interpreted as a dipole or electrostatic effect (*2*, *3*) or in terms of donor and acceptor properties, or as contributions of ionic resonance structures to the activated complex (*4*, *5*). The principle is simply: If the reacting radical (minus one electron) corresponds to a relatively stable positive ion, and if the product radical (plus

Table 2. Second Order Rate Constants for Additions of Radicals to Monomers at 60°[a]

Monomers	Radicals			
	$R-CH_2-\overset{\phi}{\underset{H}{C}}\cdot$	$R-CH_2-\overset{CO_2Me}{\underset{Me}{C}}\cdot$	$R-CH_2-\overset{CO_2Me}{\underset{H}{C}}\cdot$	$R-CH_2-\overset{OAc}{\underset{H}{C}}\cdot$
Styrene ($H_2C=CH\phi$)	145	1520	11500	~200000
Methyl methacrylate ($H_2C=CMeCO_2Me$)	278	705		~140000
Methyl acrylate ($H_2C=CHCO_2Me$)	194		2090	11500
Vinyl acetate ($H_2C=CHOAc$)	3	35	230	2300

[a] The original table of Mayo and Walling (*5*) is modified in Walling (*6*) by using new values of some propagation constants.

one electron) corresponds to a relatively stable negative ion (or vice versa), then reaction is facilitated.

Additions of Radicals to Double Bonds

Table 2 gives second order rate constants for additions of four kinds of radicals to four kinds of monomers (*5*, *6*). The rate constants for reactions of each monomer with the corresponding radical come from photopolymerizations. The other rate constants come from copolymerization data. The first value in the table gives the rate of polymerization of styrene in mole/l/second.

$$-d[M]/dt = 145[M\cdot]\,[M]$$

Thus, in pure (8.4 *M*) styrene each polymer radical adds styrene monomer at the rate of about 1200 steps per second.

Each column of figures gives the rate constants for reactions of the monomers at the side with the radical at the top. With any radical, styrene is 50 to 100 times as reactive as vinyl acetate. Styrene has a phenyl group conjugated with the double bond, and is the monomer which is converted to the most stable radical. Vinyl acetate is least reactive because the acetoxy group contributes least to resonance stabilization of either monomer or radical.

Each row of figures gives the rate constants for reactions of the radicals at the top with the monomer at the side. With any monomer, the vinyl acetate radical is about a thousand times more reactive than the styrene radical. Thus, the monomer with the least reactive double bond is converted to the most reactive radical (least resonance stabilization), and the monomer with the most reactive double bond is converted to the least reactive radical (most resonance stabilization). The low propagation constant in pure styrene shows that the contribution of resonance stabilization of the radical is more important in chain propagation than conjugation in the monomer (and potential resonance stabilization in the radical to be formed). The corners of Table 2 show that the fastest reaction is about a hundred thousand times faster than the slowest reaction. No comparable data are available for nonpolymer systems.

Irregularities in data in Table 2 are due to polar effects. While these are brought out very clearly by other copolymerization data (*2–6*), I shall use chain transfer (radical displacement) data to illustrate polar effects.

Radical Displacement Reactions

Table 3 compares the rates of reaction of each of three solvents with five polymer radicals (*7*). The radicals are listed in order of their rates of reaction with toluene. The same order applies to triethylamine but not to carbon tetrabromide. The radical from triethylamine, $MeCHNEt_2$, is classed as an electron donor because, by loss of an electron, it becomes a stable ammonium ion. In contrast, the radical from carbon tetrabromide, $Br_3C\cdot$, is classed as an electron acceptor because, on gaining an electron, it becomes a fairly stable Br_3C^- ion. The acrylonitrile radical, an electron acceptor, reacts best with the solvent which becomes the best donor radical (triethylamine). The styrene and vinyl acetate radicals, electron donors, react best with the solvent which becomes the best acceptor radical (carbon tetrabromide).

A comprehension of radical chemistry requires understanding how polar and resonance effects combine or cancel. Few quantitative data are available outside the field of vinyl polymerization. Some interesting attempts have been made to apply quantitative treatments to the polar and resonance effects (*3*, *8*).

Interactions of Radicals

Table 4 brings out polar effects in reactions of two radicals. This table gives the second order rate

Table 3. Second Order Rate Constants for Chain Transfer with Solvents at 60°

Polymer radical	Solvent		
	Toluene	Et_3N	CBr_4
Vinyl acetate	773.	137.	1440.
Me acrylate	56.5	83.6	8.6
Acrylonitrile	≥4.9	≥50.	≥0.15
Me methacrylate	0.73	0.30	1.00
Styrene	0.22	0.12	3.9

Table 4. Rate Constants ($\times 10^{-7}$) for Chain Termination at 60°[a]

Polymer radical	Self termination	Termination with styrene
Styrene	0.030	0.030
Bu acrylate	0.001	1.6
Me acrylate	0.47	12.
Me methacrylate	1.8	6.

[a] Constructed from Tables 3.3 and 4.11 in ref. (*6*).

Table 5. Relative Reactivities of Monomers Toward Styrene Radicals and Ions[a]

Monomers	Relative reactivities		
	$R—CH_2—\dot{C}H\phi$	$R—CH_2—\dot{C}H\phi$	$R—CH_2—\bar{C}H\phi$
Chloroprene	0.1	10.	
2,5-Dichlorostyrene	0.07	3.	
p-Chlorostyrene	0.3	1.3	
Isoprene	1.	1.3	
Butadiene	0.2	1.3	1.
α-Methylstyrene	6.	1.1	
Styrene	1.0	1.0	1.0
p-Methoxystyrene	>50.	0.9	
Methyl methacrylate	<0.01	0.9	>100.
Methacrylonitrile	<0.01	0.8	>400.
Methyl acrylate		0.6	>500.
Acrylonitrile	<0.01	0.3	>1000.
Vinylidene chloride	<0.01	0.2	<0.01
Isobutylene	3.	0.1	
Vinyl acetate	<0.01	0.02	<0.01
Vinyl ethers	>50.	0.01	<0.01

[a] Constructed mostly from Tables 17, 19, and 20 in Mayo and Walling (*5*).

constants at 60°C for interactions (by disproportionation, coupling, or both) for four polymer radicals with themselves, and with polystyrene radicals. The constant, 0.030×10^7 for styrene means that to maintain a concentration of 10^{-3} molar sytrene radicals in a solution, these radicals would have to be supplied continuously at the rate of 0.6 mole/l/second. In other words, radicals react fast, even in dilute solution, and their reactions would be difficult to study by ordinary methods. Note that each kind of radical reacts with styrene radical at least three times as fast as it reacts with itself, even though styrene by itself produces one of the less reactive radicals. This effect is at least partly polar. Again, vinyl polymerization provides the best data, perhaps the only data, in the liquid phase.

Reactions of Organic Ions

Polymerization can also tell us about organic ions. Base-catalyzed vinyl polymerizations involve negative organic ions rather than free radicals. Polymerizations by strong acids and Friedel-Crafts catalysts involve positive organic ions.

Table 5 shows the relative reactivities of several monomers toward the ion or radical in polymerizing styrene (on basis of 1.0 for styrene). All monomers have a measurable reactivity toward styrene radical, but those which are most reactive toward one kind of ion usually are unreactive toward the other kind. Notable exceptions are styrene, butadiene, and some of their derivatives. In general, monomers which are most reactive toward a negative styrene ion become the most stable negative ions, and monomers which are most reactive toward a positive styrene ion become the most stable positive ions. Further, monomers which are most reactive toward positive ions have a strong tendency to alternate in free radical copolymerization with monomers which are most reactive toward negative ions. For example, in the copolymer formed by a free radical mechanism at 75° from an equimolecular mixture of α-methylstyrene and acrylonitrile, about 91% of the α-methylstyrene units are followed by acrylonitrile units, and about 94% of the latter are followed by α-methylstyrene units.

The relations among reactions with ionic and free radical intermediates, which have been discussed here, are basic to a large portion of organic chemistry. Now, and for some time to come, these relations are best illustrated by polymerization data. Polymerization techniques offer the easiest route to additional data.

Laboratory Applications of Polymer Chemistry

Polymer chemistry, perhaps, can lend interest even to some high-boiling oils and tars appearing in organic preparations. Michael and Friedel-Crafts condensations of unsaturated compounds are special cases of ionic polymerizations. Polymerization conditions, which would give exclusively high polymers (gunk to the uninformed chemists), have been adjusted in these condensations to emphasize the formation of low molecular weight products (telomers).

Finally, I wish to point out that there are innumerable simple experiments in polymer chemistry which will permit students to make quantitative comparisons of reactivities of both saturated and unsaturated compounds toward both radicals and ions.[1] Table 5 only suggests what might be done to correlate structure and reactivity in organic chemistry. Laboratory work along these lines will contribute to knowledge of both polymer chemistry and organic chemistry.

[1] Relative reactivities of unsaturated compounds are determined by copolymerization. Representative procedures are described by F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944); C. G. Overberger, L. H. Arnold, and J. J. Taylor, *J. Am. Chem. Soc.*, **73**, 5541 (1951); in ref. (*5*); and on page 27 in ref. (*3*). Complete removal of solvents and unreacted monomers from polymer before analysis is not stressed sufficiently in ref. (*3*). A simple alternative method is to dry the polymer as a film (about 0.2 g of polymer spread over the bottom half of a 125-ml conical flask) by warming at reduced pressure. Relative reactivities of saturated compounds are determined from transfer constants of solvents. Representative procedures are described by R. A. Gregg and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 2373 (1948); F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 3689 (1948); G. F. Endres and C. G. Overberger, *J. Am. Chem. Soc.*, **77**, 2201 (1955). The determination of molecular weights from solution viscosities is indicated by P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, 1953, p. 308, and also by ref. (*8*).

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The Geometry of Giant Molecules

The molecules I wish to discuss are best described as molecules put together as very long, chain-like structures, built up of very many similar or even identical units. Such molecules are called linear polymers. Their molecular weight may in many cases exceed 1,000,000. In an extended form, their molecular dimensions may be of the order of 5 to 10 Å (an Ångstrom unit is 10^{-8} centimeters) in diameter and 1000 to 10,000 Å long.

As a class, these compounds include an extremely varied and exceedingly important group of substances, such as starch, cellulose, proteins, nucleic acids, rubber, nylon, dacron, polystyrene, polyethylene, polyvinyl chloride, and many other plastics.

The interesting, useful, and in fact vitally important chemical and physical properties of these substances are influenced significantly by features of the molecules which can affect the geometrical arrangements of these long chains. Thus, it now appears that there are at least three principal possibilities for the special arrangement of such molecules, i.e., (*a*) extended, rigid, rodlike, (*b*) randomly coiled, like a tangle of string, and (*c*) regular helical coils, resembling a coiled spring (see Fig. 1).

Figure 1. Shapes of linear polymer molecules.

It turns out that there are several factors related to the detailed structure of the units of these long-chain molecules which significantly influence the geometrical arrangement. One factor is the flexibility, or more precisely, the rotatability of one unit with respect to its neighbor about the bond joining them, and whether there is a preferred rotational arrangement. The different geometric arrangements of molecules due to rotations around bonds are now commonly called *conformations* of the molecule.

Another extremely important factor arises if the units of which the chain is constructed are *asymmetric*, i.e., if they can differ from one another as a right hand differs from a left. This difference in geometry, described as a difference in *configuration*, leads to the interesting possibility of building chains of all right-handed units, of all left-handed units (*isotactic*), of regular alternations of such units (*syndiotactic*) or of random sequences of such units (*atactic*).

A third factor of great importance to the physical properties of polymeric substances is the "stickiness" of the chains, i.e., the energy of van der Waals and other intermolecular forces which tend to hold one chain to another. A simple analogy for such a difference might be a bowl of hot spaghetti (weak forces) or of cold spaghetti (stronger forces),

Let us now consider some specific examples of polymer molecules, natural and synthetic, of differing geometric arrangement and examine how these factors influence their properties.

Polyethylene

One of the simplest synthetic polymers, polyethylene, is made by catalytic combination of thousands of small ethylene molecules (C_2H_4) into a giant, linear polymer.

$$n\,CH_2{=}CH_2 \longrightarrow -(CH_2{-}CH_2)_n-$$

Ethylene — Polyethylene

Linear polyethylene is a moldable plastic, melting near 140°C. Study of crystalline polyethylene by X-rays reveals that, in the crystalline state, the chains are in an extended, rodlike form (Fig. 2).

If one could place one's eye as indicated so as to

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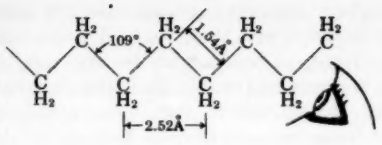
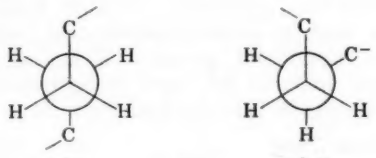


Figure 2.

get a view along the axis of one of the carbon-to-carbon bonds in this extended zig-zag chain, one can represent the situation as in the second figure (Fig. 3). The circle represents the closer carbon atom and the three full lines, three of the valence bonds of this carbon. This atom is bound to another immediately behind it by a fourth valence. The three other valences of the back carbon are represented by the small lines, bisecting the valences on the front carbon. From other information on smaller molecules, it is known that this *trans* conformation (Fig. 3*a*), with the larger CH_2 group on the front carbon in between the small hydrogens on the back, and vice versa, is energetically favored over any other rotational arrangement such as the *skew* conformation (Fig. 3*b*). These extended, rodlike



trans ≫ *skew*

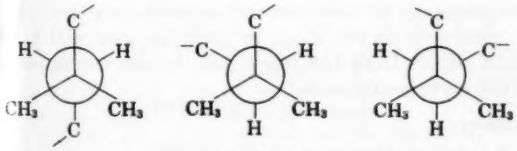
Figure 3a. Figure 3b.

molecules pack together in neatly ordered, crystalline arrays, much like uncooked spaghetti in its box. This regular array is stable and resists dissolution or distortion at temperatures below the melting point of 140°C.

Butyl Rubber

The hydrocarbon isobutylene (C_4H_8) which is a chemical relative of ethylene, has also been polymerized to give high molecular weight linear polymer.

If one looks along the axis of a carbon-to-carbon bond in this chain, the following three arrangements appear equally likely.



trans(linear) ≃ *skew* (left) ≃ *skew* (right)

Figure 4. Figure 5a. Figure 5b.

For the backbone carbon atoms of the polymer chain, Figure 4 represents the extended *trans* zig-zag arrangement or conformation. For these atoms, Figures 5*a* and *b* represent bent or coiled arrangements of the chain. In this case, the rear chain carbon (C′)

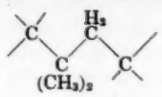
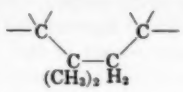


Figure 4(side view)

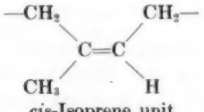


Figures 5(side view)

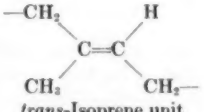
may be between the two methyl (CH_3) carbons in the front (Fig. 3*a*) or between a methyl carbon and the front chain carbon (Fig. 5*a* and *b*). Contrary to the polyethylene case, these three arrangements or conformations are very nearly equal in energy (and therefore probability). Since there is no preference for a left or right coil, this long chain molecule assumes a randomly coiled arrangement, intertwined with other such random coils. Since the forces between chains in the case of polyisobutylene are weak, the "fluid" assembly of giant molecules can deform under stress or strain. For example, the molecules can elongate or uncoil in the direction of pull. However, as soon as the stress is removed, the uncoiled portions will return to the preferred randomly coiled arrangement at any temperature sufficient for thermal agitation of units to overcome weak attractions between chains. Thus this property of rubbery elasticity is dependent on temperature and can be "frozen out" at very low temperatures.

Natural rubber

Natural rubber similarly is constructed of a unit (C_5H_8) which prefers a bent or randomly coiled arrangement.



cis-Isoprene unit (rubber)

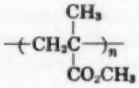


trans-Isoprene unit (gutta percha)

Under stress these may also assume a more linear arrangement. In fact, the stretched rubber, with the chains held in a more or less linear pattern, can fit together into an orderly crystalline array, as indicated by X-ray studies of stretched natural and butyl rubber. Unless the temperature is very low, these "crystallized" regions of stressed rubber "melt" as soon as the stress is relaxed, reverting to the randomly coiled structure.

Polymethyl Methacrylate

Polymethyl methacrylate (Lucite or Plexiglas) is similar to polyisobutylene in some respects, except one methyl group (CH_3) is replaced by a methyl ester group (CH_3CO_2).

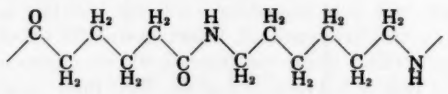


The molecular geometry is somewhat similar to that of polyisobutylene and the molecules are usually in a randomly coiled arrangement. The main influence the oxygen has is to increase the "stickiness" of the chains, i.e., the attraction between chains. One important consequence of this is that the thermal energy at room temperature is *not* sufficient to overcome this "stickiness" so that assemblies of randomly-coiled poly-

methyl methacrylate molecules are solid, undeformable plastics until heated. At temperatures above 100°C, this polymer becomes rubbery, it can be deformed and, if quickly cooled in the deformed state, will resolidify with some of the chains stretched out of the preferred randomly coiled arrangement. If the new form is then later again heated to over 100°C, the chains will revert to the stable coil, and the piece will again assume its earlier shape. This is known as "plastic memory."

Polyamides

Nylon is a polymer of somewhat different structure and its repeating unit is represented as



Notice that portions of the chains resemble polyethylene units and would prefer an extended *trans* zig-zag arrangement. However, the positively charged hydrogen of an NH group in one chain has a strong attraction for the negatively charged oxygen in an adjacent chain. The "stickiness" of the chains thus does not permit the randomly coiled molecules in molten nylon easily to migrate into an ordered crystalline arrangement on cooling (see Fig. 6). By stretching or

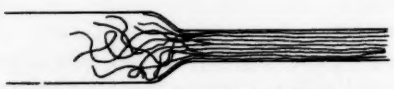
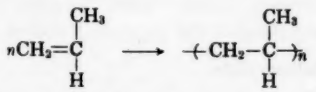


Figure 6.

"cold-drawing" the original randomly oriented fiber, the chains become oriented in the direction of the stretch, the fiber "necks-down" to about one-third the original diameter and becomes crystalline, much stronger, less elastic, and more resistant to solution and chemical attack.

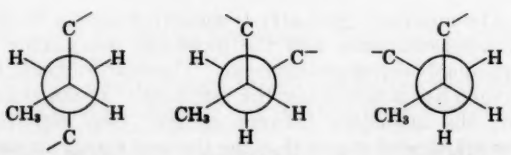
Polypropylene

In polypropylene, prepared by combining many molecules of propylene (C_3H_6), an interesting new geometrical possibility arises.



Referring back to Figures 3*a* and *b*, polypropylene would be represented by replacing one of the methyl groups on the front carbon by hydrogen. Notice that one can replace either the left or the right methyl group. Figures 7, 8, and 9 represent the case if we replace the left-hand methyl by hydrogen.

There are three similar arrangements for a methyl



trans (linear) ≃ *skew* (right) ≫ *skew* (left)

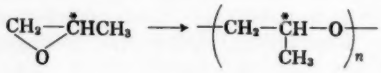
Figure 7. Figure 8. Figure 9.

on the right. Actually, in this case the form represented by Figure 9, with the C in back between two large groups in front, in contrast to the situation in Figures 7 and 8, is much less stable than the first two forms. Therefore, this structure will have about an equal chance of being *trans* or always *skew* right. However, the older methods of polymerizing propylene gave equal probabilities of the structure with the methyl group right or left, and these units were randomly distributed. The molecules could thus coil either right or left, assuming a randomly coiled arrangement, and like polyisobutylene, exhibit rubberlike properties.

Professor Natta in Italy recently discovered that new catalyst systems could give propylene units selectively with the methyl group always in one direction. These molecules then tend to coil always in the same direction and actually assume a regular helical spiral arrangement. This regular helix is stiff and rodlike, and packs into crystalline patterns neatly, melting at 170°C. This new form of polypropylene, rather than being a rubbery, soluble material, is an excellent plastic and forms strong and insoluble fibers. Polymers of this kind, with asymmetric units all right-handed or left-handed (*isotactic*), promise to be of major industrial significance. Actually, many natural polymers, such as protein, nucleic acid, and starch, have this remarkable property of having all their asymmetric units of the same configuration, and of preferring a regular helical coil arrangement.

Polypropylene Oxide

About the same time that Professor Natta discovered isotactic polypropylene in Italy, chemists at Dow and the University of Pennsylvania reported a new form of polypropylene oxide.



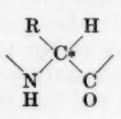
Here also there is a marked difference between the atactic material, which is soft and rubbery at room temperature, and the isotactic material, which is a crystalline, fiber-forming solid, melting at 70°.

The case of propylene oxide differs from that of propylene in two significant ways. First, the monomer itself is asymmetric and can be prepared in *d* and *l* forms. Second, the isotactic polymer contains genuine asymmetry and can be obtained in optically active form.

For polypropylene, the isotactic polymer will have a plane of symmetry in the middle of the chain and is therefore an optically inactive *meso* form. One might also consider the asymmetric atoms of isotactic polypropylene to be examples of *pseudoasymmetry*, since, as viewed from the atom in question, one end of the chain differs from the other only in the configuration of the asymmetric centers.

Proteins

Proteins, which are most important substances to the life process, are also generally linear polymers, built from the following "peptide" unit.

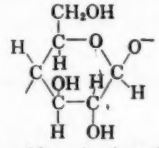


Notice that the carbon marked with the asterisk is similar to the asymmetric atoms of polypropylene oxide chains. It turns out that in natural proteins, the arrangement is always the *levo*-configuration, or left-handed arrangement. This again leads to preference for a helical-coiled arrangement (Fig. 10). These helical coils can actually exist in several modifications, with different numbers of "peptide" units per coil. The coil is "cemented" together by the strong attraction of the hydrogen of an >NH group in one turn of the coil, with the oxygen of a >CO group of an adjacent turn.

Many of the vitally significant properties of proteins depend on these helical structures. One process of "denaturation" of proteins involves procedures which disrupt the forces holding the helix intact, allowing it to assume a more randomly coiled arrangement.

Carbohydrates

The structural unit of cellulose is a 4,β-glycopyranoside unit. A native cellulose molecule may be constructed as a linear chain of 10,000 or more of such molecules joined regularly, end-on-end, at the unfilled valence bonds indicated at either end of this unit.



4,β-Glucopyranoside unit of a cellulose molecule

The ring holds this unit in a reasonably rigid arrangement. The attachment of additional units at opposite ends and on opposite sides of this ring tends to make the long-chain aggregate of these units a rigid, rodlike molecule. It is the aggregates of these long-chain, rodlike, cellulose molecules which make cellulose a fiber-forming material. Since the hydroxyl groups in each unit, through hydrogen bonding, have a strong attraction for adjacent hydroxyl groups in neighboring

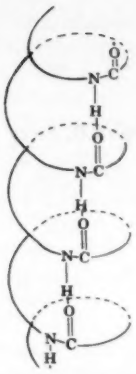
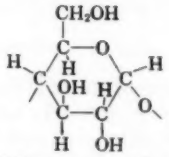


Figure 10. Representation of hydrogen bonding between adjacent coils of a protein helix.

chains, the aggregate of cellulose chains resists solution and melting.

Starch is very similar to cellulose, except that the linkage of units at opposite ends of the glucopyranose units is on the same rather than the opposite side of the ring. Because of this, the starch molecule can assume a regular helical coil, with about six glucose units per turn of the helix. The strong hydrogen bonding between the free hydroxyl groups of each glucose unit then occurs between units in adjacent coils of the same helix, and starch, therefore, is not nearly so resistant to solution. The remarkable blue color formed when starch is exposed to iodine has been shown to involve iodine molecules slipping into the "hole" down the center of the coil, which happens to have exactly the right diameter to accommodate iodine molecules.



4,α-Glucopyranoside unit

The Ida and Henry Schuman Prize in the History of Science

An annual award of $250 has been established by Henry and Ida Schuman of New York City for an original prize essay in the history of science and its cultural influences. This competition is open to undergraduate and graduate students in any American or Canadian college, university, or institute of technology. Papers submitted for the prize competition should be documented. It is hoped that the prize-winning essay will be suitable for publication in *ISIS*, the journal of the History of Science Society.

Papers submitted for competition should be sent to the Chairman of the Prize Committee, Professor A. H. Dupree, Department of History, University of California, Berkeley 4, California. Inquiries about the competition may also be addressed to Professor Dupree. To be eligible for consideration, papers must be received on or before July 1, 1959.

John D. Ferry
University of Wisconsin
Madison

Polymer Chemistry in the Elementary Physical Chemistry Course

The teacher of elementary physical chemistry is confronted by an increasing number of highly specialized topics which should be included in his course, and yet the classical fundamental subject matter cannot be sacrificed. Some new material, such as polymer chemistry, can be advantageously introduced as illustrations of basic concepts, without departing from the customary development of the subject. At the University of Wisconsin, where the physical chemistry courses are undergoing continual revision by the authors of our lecture (*1*) and laboratory (*2*) textbooks and their colleagues, polymers are mentioned in a variety of contexts. Thus the students become aware of the existence of macromolecules, and are given some hint of their characteristic properties, as well as of the opportunities for research in this field and the importance of polymer technology. As may be seen from the following examples, polymers provide in certain cases more apt and timely illustrations than can be drawn from ordinary substances of low molecular weight.

X-ray Diffraction

The elementary exposition of structure determination by X-ray diffraction is inevitably limited to very simple cases such as the alkali halides, and even here the quantitative treatment must be incomplete. It is useful to supplement the classical material with examples which do not involve quantitative calculations and complicated projective geometry but permit drawing qualitative conclusions by inspection. The macromolecular chemist is able to gauge the degree of crystallinity and the degree of orientation of a polymer sample from a glance at its diffraction pattern. The manifestation of crystallinity runs the scale from a typical liquid pattern with one or two blurred halos to a Debye-Scherrer pattern with sharp rings; the manifestation of orientation runs from a Debye-Scherrer to a von Laue pattern (*3*). The student will recognize the classical patterns as limiting cases and become intuitively familiar with the reciprocal relation between spacing on the pattern and spacing in the structure.

Chemical Kinetics

The classical example of a chain reaction is the formation of hydrogen chloride from the elements. But another useful example is polymer synthesis by a free radical addition process, which is graphic in the sense that the reaction leaves a material record of itself—a chain molecule. The nature of the steady state, in which the number of growing chains is approximately constant and the initiation and termination rates are equal, is readily visualized. The suppression of chains by inhibitors and free radical scavengers, and the phenomenon of autoacceleration, in which the consumption of monomer speeds up toward the end when growing chains have trouble reaching each other to accomplish termination, demonstrate the sensitivity of chain reactions to varying conditions. Free radical kinetics is discussed in more detail in other papers in this issue (*4*).

Rubberlike Elasticity and Thermodynamics

The concept of a network of wriggling, writhing flexible threadlike molecules adds a new type of thermal motion to the classical examples of translation, vibration, and rotation. Picturing the structure of soft vulcanized rubber in these terms readily explains the retractive force of a stretched elastomer and the fact that this force, attributable to the violence of the thermal motion, is directly proportional to the absolute temperature.

Simultaneously, examination of the stretched rubber from the point of view of thermodynamics provides a graphic illustration of the nature of entropy. External distortion of the network imposes restrictions on the assortment of configurations which the individual strands can assume, so the system is less random and the entropy is decreased. For a "perfect" rubber, there is no change in enthalpy, and the free energy of stretching is $\Delta F = -T\Delta S$, a positive quantity proportional to T. The increase in free energy—the capacity to do useful work—is in fact the work of stretching, which can be recovered reversibly (*5*).

Osmotic Pressure

Among the colligative properties of solutions, osmotic pressure has usually been cited as primarily of historical interest; one is a little apologetic about going back as far as Pfeffer or Berkeley for examples of data. But illustration with data on polymer solutions has contemporary relevance; for the method is widely used to determine molecular weights and to study deviations from ideality (*6*). Moreover, this illustration demonstrates how the different colligative properties can in practice supplement each other even though in principle they give identical information. For solutes of low molecular weight, osmotic pressure is inferior to freezing-point lowering because of the difficulty of obtaining selective membranes and the rather large

Presented as part of a Symposium on Instruction in Polymer Chemistry, sponsored jointly by the Division of Polymer Chemistry and the Division of Chemical Education at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

pressures developed even at low weight concentrations. For macromolecular solutes, the situation is reversed; freezing-point depressions are vanishingly small at moderate concentrations, but osmotic pressures fall in just the right range for convenient measurements, the membrane selectivity is a simple matter to achieve. Besides, the presence of traces of impurities of low molecular weight can completely falsify freezing-point lowering measurements, but do not affect osmotic pressure to any substantial degree because they equilibrate across the membrane.

Laboratory Experiments

Two physical chemistry experiments involving high polymers have been in use at the University of Wisconsin for a number of years (*2*). In one, intrinsic viscosity measurements are used to estimate the molecular weight of a polymer sample and to illustrate the effect of solvent power on the average dimensions of a randomly coiled molecule (*7*). In the other, somewhat more difficult for the average student, osmotic pressure measurements are made to determine the number-average molecular weight, using a simple osmometer of the Schultz-Wagner type (*8*), with membranes of alkali-swollen cellophane.

Additional experiments are being introduced on a trial basis. Viscosity measurements on simple liquids by the traditional Ostwald method are supplemented by measurements with the falling sphere method on a polymeric oil, to give the student some acquaintance with a viscosity of a very different order of magnitude. The thermodynamics of rubberlike elasticity is investigated by stress-strain measurements at various temperatures between 0° and 60°, where a length of $^1/_8$-in. pure gum (transparent) rubber tubing is stretched in series with a spring balance. From the measurements of tension at different temperatures at constant length, the student finds that the elastic energy is indeed approximately proportional to T, with the thermodynamic consequences outlined above. From measurements of tension at different lengths at constant temperature, he can confirm the non-Hookean behavior predicted by the statistical theory of rubberlike elasticity (*5*), and estimate the average molecular weight between cross-links in the vulcanized network. A more detailed description of this experiment will be published in THIS JOURNAL at a later date.

Conclusion

The example cited show how some aspects of high polymer chemistry can be introduced to undergraduate students as part of their basic training in physical chemistry. It is hoped that undergraduate courses will increasingly include allusions such as these to macromolecules, to prepare students for the important role which polymers play in current research and development.

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Division of CHEMICAL EDUCATION

American Chemical Society

GRANT W. SMITH, Chairman of the Division of Chemical Education, has made the following committee appointments. These appointments all run through December of the year indicated.

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Fred W. Billmeyer, Jr.
University of Delaware and
E. I. du Pont de Nemours & Co.
Du Pont Experimental Station
Wilmington, Delaware

A Graduate Curriculum in Polymer Chemistry

Instruction in graduate courses in polymer chemistry began in the fall of 1958 at the University of Delaware for approximately the eighteenth year. It is interesting to see that, in this institution at least, the stage has been reached where details of the beginnings of instruction in polymer science are becoming obscure. Considerable subject matter now called polymer chemistry was taught in a course designated colloid chemistry by Dr. E. O. Kraemer as early as 1941. The first courses under titles involving polymer chemistry were taught in 1944 in chemical engineering by Dr. G. E. Landt, and about 1945 in the chemistry department by Dr. H. M. Spurlin. Since then courses have been given almost every year, in the University Extension Division by Professor Elizabeth Dyer, Dr. H. A. Pohl, and the author.

At the present time, as for the last seven years, four courses in polymer chemistry are offered in the Extension Division in successive semesters. The cycle of four courses covers successively the properties of plastics (under the title Organic Chemistry of High Polymers), the properties of fibers and elastomers, the physical chemistry of polymers, and the kinetics of polymerization. Typically, these courses consist of 15 two-hour evening lectures, one lecture being given each week.

In addition to these courses, the demand for instruction is sufficiently great to have a Saturday course in the organic chemistry of polymers taught on campus every second year. This course covers in one semester the material given in the two evening courses on the properties of plastics and of fibers and elastomers. It is given in the years when the evening courses on physical chemistry and kinetics are offered.

In addition to its full-time graduate students, the University of Delaware enrolls many part-time students at the graduate level. These students may enter the Graduate School as candidates for advanced degrees or may enroll as students in the Extension Division. Graduate school students, both full time and part time, made up about 60% of the enrollment in polymer courses over the past seven years. While exact figures are not available, it is estimated that not over a fifth of the enrollment consisted of full-time graduate students.

Thus by far the majority of the students taking these polymer courses are employed in industry and continuing their education on a part-time basis. Some are candidates for advanced degrees, while others already hold such degrees and take the courses solely for information. It has been observed that both these groups consist largely of chemists and engineers employed in the plastics, fibers, elastomers, and petroleum industries within an area extending as far as a hundred miles from the university. The educational problems of these men and women are of particular interest, for they are the chemists who, as students, had little or no contact with polymer chemistry, yet are active in this expanding field.

The enrollment in the polymer courses taught in the Extension Division over the last seven years ranged from a high of 46 to a low of 12, with an over-all average of 30 students per course. The more descriptive courses covering the properties of plastics and the properties of fibers and elastomers were about half again as popular as the more theoretical courses of physical chemistry and kinetics. About a quarter of the students were auditors; the rest participated in the examinations and received Graduate School or Extension Division credit.

Content of the Courses

Physical Chemistry of High Polymers. Table 1 reproduces part of the assignment sheet for the course in the physical chemistry of polymers. After an introductory lecture, this course is divided into three sections. The first deals with such polymer properties as crystallinity and melting, the glass transition, and polymer structure as deduced from X-ray diffraction and infrared absorption spectroscopy. The second section covers the thermodynamics of polymer solutions, including fractionation and molecular weight determination. In the final section are discussed rubber

Table 1. Prospectus for Physical Chemistry of High Polymers

Introduction
Chemical Bonds and Molecular Forces
Crystallinity, Orientation, and Transitions
Crystal Structure of Polymers
Infrared Analysis and Polymer Structure
Conformation of Polymer Chains in Solution
Thermodynamics of Polymer Solutions
Solubility and Fractionation
Colligative Methods of Molecular Weight Determination
Light Scattering
Solution Viscosity and Molecular Size
The Ultracentrifuge
Rheology
Kinetic Theory of Rubber Elasticity
Viscoelastic Properties of Polymers

Presented as part of a Symposium on Instruction in Polymer Chemistry, sponsored jointly by the Division of Polymer Chemistry and the Division of Chemical Education at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

elasticity and polymer melt properties such as viscoelasticity and rheology.

Polymerization Kinetics. The contents of the course in kinetics are similarly outlined in Table 2. This

Table 2. Prospectus for Polymerization Kinetics

Linear Condensation Polymerization
Three-Dimensional Condensation Polymerization
Kinetics of Addition Polymerization
Absolute Reaction Rates
Thermochemistry of Polymerization
Copolymerization Kinetics
Reactivity and Structure of Monomers and Radicals
Structure and Composition of Copolymers
Block and Graft Polymerization
Rates, Molecular Weights, and Distributions
Emulsion Polymerization and Redox Initiation
Diene and Divinyl Polymerization
Ionic Polymerization
Polymerization to Stereospecific Polymers
Polymer Degradation

course encompasses condensation polymerization, addition polymerization by free radical and ionic mechanisms, the production of sterically ordered polymers, and polymer degradation.

Organic Chemistry (Plastics), Fibers and Elastomers. The contents of the two more descriptive courses are briefly outlined in Table 3. Basically, these courses cover the production, physical and chemical properties,

Table 3. Outlines of Organic Chemistry of High Polymers and of Fibers and Elastomers

Polymer Processing
Properties of Vinyl Polymers
Properties of Condensation and Other Polymers
Structure and Properties of Fibers
Conversion of Polymers into Fibers
Properties of Fibers
Structure and Properties of Elastomers
Vulcanization and Reinforcement
Properties of Elastomers

and end uses of commercially important plastics, fibers, and elastomers. Considerable emphasis is placed upon the relation of polymer properties to molecular structure. The polymers are covered by type; for example, in the category listed as "Properties of Vinyl Polymers" fall lectures on polystyrene, the acrylics, polymers derived from vinyl acetate, chlorine-containing polymers, fluorine-containing polymers, and hydrocarbon polymers including polyethylene.

Level of Teaching

In deference to the mixed nature of the student enrollment, it has been found advisable to temper the mathematical rigor which might be expected in courses on the physical chemistry and kinetics of polymer systems, by the inclusion of considerable descriptive material. The majority of the students, faced with the practical problems of dealing with polymers in industry, are initially concerned with the behavior of these materials in experiments, and the reasons for this behavior. Later they are able to explore for themselves the rigorous derivations of the equations which are applicable. While it may be that these courses do not furnish as strict a discipline for the student as some, it is believed that their emphasis on practicality more nearly answers the needs of the students.

In the more descriptive courses dealing with fibers and elastomers, the emphasis tends toward a more theoretical treatment than might be anticipated. Thus there is considerable overlapping between the two sets of courses: on the one hand, polymer properties are described to illustrate principles of physical chemistry or kinetics, while on the other hand these principles are used to illustrate the relations between polymer properties and structure.

Similarly, there is considerable overlapping between the evening and Saturday courses. The latter is of particular interest to full-time graduate students in fields other than polymer chemistry, who want an introduction to polymer theory even though they cannot afford the time for the full sequence of evening courses. Although the Saturday course is catalogued as the Organic Chemistry of High Polymers, it contains as much physical chemistry as seems possible.

Physical chemistry, organic chemistry, and calculus are prerequisites to the courses. Although designed for first year graduate students, they have been successfully completed by well prepared senior undergraduates.

When the cycle of four polymer courses was begun, various texts were used with less than complete satisfaction. None was found which offered an up-to-date treatment reasonably near our requirements, and in some areas there was simply nothing available. In an effort to fill this gap, lecture notes were expanded into a textbook of polymer chemistry.[1] The book has proved quite satisfactory in these courses, and has achieved a gratifying measure of success elsewhere. It is meant to be supplemented by reading assignments in more advanced or detailed works and in the original literature.

Other Types of Instruction

Soon after lecture courses in polymer chemistry were initiated at Delaware, a laboratory course in the methods of polymer chemistry was taught by Professor Dyer for about three years. This course dealt largely with polymerization processes with their typical requirements of relatively long periods of constant attendance, careful control, and extreme chemical purity. It was, however, found to consume a large amount of the time of both students and instructor. Consequently, it was given up in favor of teaching what methods the student needs through his research problem. No attempt has been made in the university to institute a formal course of physical chemical experiments with polymers, though this field would seem more amenable for the establishment of a laboratory course, if the proper apparatus is available.

Research in polymer chemistry is considered an important part of the instruction in this field. To date there have been, in the chemistry department at Delaware, over 35 M.A. and Ph.D theses dealing with some aspect of polymers. Typical fields include the properties of nucleic acids, the oxidative degradation of polymers, studies of polyurethanes, mucous polymers,

[1] Billmeyer, F. W., Jr., "Textbook of Polymer Chemistry," Interscience Publishers, Inc., New York, 1957.

and "vulcanized" fibers, and investigation of molecular weight and chain branching.

While one might hope that, ultimately, much of the descriptive material now taught in these polymer courses could be incorporated into the undergraduate curriculum, this change in curriculum does not appear probable in the near future. All branches of chemistry are expanding tremendously. Courses have become stuffed almost to the bursting point. At the same time, there is a wider recognition of the need for more exposure of the technical student to the humanities, as well as for more independent study in his specific field. Thus, it seems likely that a continuing need may be anticipated for the broad coverage in moderate detail offered in our graduate curriculum in polymer chemistry.

Acknowledgment

The experience of Professor Elizabeth Dyer, gained through her close association with instruction in polymer chemistry at Delaware from its beginning, has proved invaluable.

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Polymer Chemistry Instruction in Small Colleges and Universities

Undoubtedly a major deterrent to more extensive instruction in the elements of polymer chemistry is the simple fact that there are relatively few true polymer chemists in academic institutions. If a polymer chemist is defined as someone who is active in research in some phase of polymer chemistry and who considers his work in the polymer field to be one of his major research interests, then one finds for the last year for which statistics are available that over half of the M.S. and Ph.D. degrees in chemistry were awarded by institutions which did not have on their staff anyone who could legitimately be considered a polymer chemist (*1*). Undoubtedly the situation with respect to B.S. degrees is even worse. Although the absence of a polymer chemist is almost universal in the smaller colleges and universities (whence the title of this article), it is also sufficiently common in the larger schools to make the problem of polymer instruction *sans* polymer chemist of general importance. The purpose of the present article is to consider briefly what the institution lacking a polymer specialist should and, more important, can do in providing polymer instruction at both the undergraduate and graduate levels. (In considering this problem we shall have reference from time to time to our personal experience at the University of South Carolina; but it should be clearly understood that we present this not as the ideal solution but rather as an example of what can be done.)

Macromolecular Topics in Elementary Organic Courses

In view of the tremendous industrial and physiological importance of macromolecules, it seems imperative that any undergraduate curriculum in chemistry include some elementary polymer instruction. There seems to be general agreement that the best way to do this is through integration of polymer material into existing undergraduate courses and that the most appropriate candidates are the courses in physical and organic chemistry. At the University of South Carolina we concentrate almost all our undergraduate polymer work in the organic chemistry course. This is dictated not by choice but by the fact that those teaching organic have had considerably more experience with polymer topics. For this reason we include with the usual organic polymer material a qualitative introduction to some aspects of the physical chemistry of high polymers. Altogether we devote about one-fourth of one semester of the organic chemistry course time to a consideration of macromolecules. We discuss those characteristics and properties of macromolecules which set them apart from covalent structures of ordinary dimension. We consider qualitatively the question of molecular size distribution and the problem of molecular weight determination (with a brief description of the principles involved in the methods commonly used). We examine in some detail the structure, synthesis, chemical modification, and properties of polymers of particular interest. These include natural polymers (cellulose, starch, and proteins); condensation polymers (Nylon, polyesters, polyurethanes, thermoset resins); addition polymers (polystyrene, polymethyl methacrylate, GR-S rubber and polyacrylonitrile). It is obvious that a coverage of this sort permits the inclusion at appropriate points of such topics as the mechanism of free radical vinyl polymerization; copolymerization; regulation of molecular weight by chain transfer; cross-linking, network formation and the properties of networks; helical structure of proteins; crystalline as opposed to amor-

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phous polymers; ionic addition polymerization. Since this is a course in organic chemistry it should be evident that many of these topics are treated only qualitatively. However, despite this fact it has been our experience that it is possible in this fashion to give students a good understanding of some of the elements of polymer chemistry. It has also been our experience that this portion of the course is received with particular interest.

We should stress that one certainly need not be a polymer chemist in order to be able to make a presentation of the sort described above at the undergraduate level. Any organic or physical chemist by short study of some of the excellent treatises (*2*) and reviews (*3*) on polymer chemistry should be able to become sufficiently familiar with the elements of the subject as they apply to his particular field to introduce macromolecular topics more effectively in his undergraduate course. The amount of personal study required to do this is not large, especially in view of the contemporary importance of the subject matter.

Polymer Chemistry at the Graduate Level

At the graduate level the school which lacks a polymer chemist faces a much more difficult problem in attempting to provide adequate polymer instruction. Doubtless there are some who feel that it is best in this situation to make no attempt to present any polymer subject matter. However, we feel that even here a considerable amount can often be done and, if the material can be presented well, it provides a worthwhile adjunct to the usual graduate program.

There seem to be two limiting approaches to providing polymer instruction at the graduate level. The first is to revise existing graduate courses in such fashion as to introduce considerably more macromolecular topics. The second is to keep the existing courses unaltered and to add a graduate survey course in polymer chemistry (usually elective but in some cases required of all graduate students). Naturally all sorts of combinations of these two limiting schemes are possible. For a school of the type under discussion the particular option chosen will be largely determined by the backgrounds and interests of those teaching the graduate program. Thus, unless there is a staff member who has had considerable prior acquaintance with polymer chemistry, a survey course is an impossibility. On the other hand, with such an individual available and the other department members macromolecular neophytes, a polymer survey course is probably the best solution. At the University of South Carolina our situation corresponds roughly to the latter case. As a result we have elected to concentrate the majority of our graduate polymer instruction in a polymer survey course. However, before discussing the nature and content of this survey course, we would like to point out some of the things that can be done under suitable circumstances to discuss a few macromolecules in the usual courses of the graduate program.

In the present symposium Price (*4*) has shown that certain stereochemical principles may be illustrated nicely by reference to various types of polymers, their structures and their properties. Since stereochemistry is usually considered at some length in advanced organic courses, the inclusion of this particular polymer chemistry in the usual graduate program would seem quite feasible. A second example comes from our own experience. We have found it very convenient in a kinetics course to employ vinyl polymerization as a model free radical chain reaction. In fact we feel vinyl polymerization is considerably better for illustrating the basic characteristics of radical chain processes than those reactions more commonly used for this purpose in textbooks, as for example the H_2-Br_2 reaction. Third, we might note that any discussion of the effect of structure on reactivity in radical reactions (as might occur in a course dealing with physical-organic chemistry) must inevitably make extensive reference to copolymerization, chain transfer, inhibition, etc., studies; for these provide, as Walling (*5*) has pointed out, the bulk of the extant data on relative reactivity in radical reactions. Fourth, in the realm of thermodynamics one can envisage that it should not be difficult to include such a topic as the thermodynamics of rubber elasticity in the latter part of the usual graduate "thermo" course. This material might be an interesting relief from the expanding gases and infinitely dilute solutions which normally monopolize the thermodynamics course. Finally, a fifth suggestion: Might not graduate courses in inorganic chemistry give increased emphasis to the polymeric nature of many inorganic substances (silicates, phosphates, etc.) and at the same time point out some of the current research efforts in the active field of inorganic polymers? These are just a few examples of what can be done, but it must be recognized that any of them demand that the instructor be thoroughly conversant with polymer chemistry insofar as it applies to the particular subject involved. It is the author's opinion that the above approach is probably the most desirable for a school without a polymer chemist, but unfortunately due to the already considerable demands on the average professor's time it is often difficult to get those unlettered in polymers to study the subject to the extent required for incorporation of polymer topics in their courses. Until there is more insistent pressure for widespread instruction in macromolecular chemistry, the activation energy for any form of professorial self-instruction is liable to remain rather high.

The alternative, as mentioned earlier, is the polymer survey course. This requires someone who has been extensively exposed to polymer chemistry in the not too distant past. In the author's case this came about through two and one-half years spent as a member of an industrial group concerned with basic research in polymer chemistry. Although his personal concern was with problems relating to the kinetics of vinyl polymerization, the backgrounds and research interests of the group as a whole encompassed most macromolecular chemistry and provided an excellent opportunity for an on-the-job general education in the principles of polymer chemistry. Since that time the author's research interests have touched on polymers only infrequently. For this reason he can no longer rightfully be considered a polymer chemist. However, it is his belief that this previous (1953–55) training in polymer chemistry still provides a sufficient back-

ground to permit the presentation of an acceptable survey course. Undoubtedly the course suffers somewhat from the fact that its instructor is no longer actively engaged in polymer research, but the alternative at present would be virtually no presentation of polymer chemistry at the graduate level. In this situation it is our feeling that half-a-loaf is definitely better than none.

We offer our survey course as an elective usually taken by Ph.D. candidates at the end of their formal course work. To date nearly all of our Ph.D. candidates have registered for the course, either for credit or as auditors, a fact which seems to indicate a general desire among graduate students for knowledge about polymers. Though we have no formal prerequisites for the course, we prefer that the student have had thermodynamics, advanced organic chemistry, and kinetics. In the survey course we try to cover a fairly wide spectrum of polymer topics. An outline of most of the major topics discussed would be as follows: kinetics and molecular weight distributions in condensation and vinyl polymerizations; copolymerization; block and graft copolymers; emulsion polymerization; molecular weight determination; polymer structure and properties; nonlinear polymers, cross-linking and gelation; chain configuration; rubber elasticity; elementary thermodynamics of dilute polymer solutions. In discussing these subjects we stress throughout the importance of the statistical approach in the solution of polymer problems. We make no attempt to examine any of these topics exhaustively, choosing rather in each case to concentrate our attention on the simple fundamentals and to stress an understanding of the basic principles and reasoning involved. Such an approach has the added advantage of keeping most of the mathematics involved within the easy grasp of all the students, although even so we have found it desirable to eliminate portions of some of the more complicated derivations. As a text we use Flory's "Principles of Polymer Chemistry" (*2b*). This permits those students who so desire to examine many of the subjects in greater depth and detail than given in the lectures. The aim of the course is definitely not to produce experts in polymer chemistry but rather to give doctoral candidates a solid introduction to macromolecules. However, it is our belief that should our students become intimately involved in polymer chemistry in their later work they will find the transition much easier as a result of having taken the survey course.

The above gives some idea of what can be done in presenting polymers in an institution that has no real polymer chemist on its staff. While it has been our intention to show that much can be done in this situation, it must be stressed that any of the above suggestions will prove inoperative in the face of sufficient faculty ignorance of polymer chemistry. Therefore, it might be appropriate to close by offering a few thoughts on alleviating this situation. First, institutions fortunate enough to be geographically contiguous to an industrial research laboratory having a polymer research group might well arrange for a member of this group to offer a polymer survey course of the sort described above for the edification of *both* students and faculty. Those not so advantageously located, if funds are available, might consider sending an interested young faculty member to one of the intensive summer polymer courses offered by at least some of the institutions which specialize heavily in polymer research. Finally, and most important, those teaching at universities where adequate polymer instruction is presently available should strongly urge all students who contemplate a teaching career to get at least some grounding in polymer chemistry while they are in graduate school, even though this subject does not seem to the student to be particularly germane to his present or contemplated research interests.

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Are Scientists Honored by Commemorative Coins?

We quote from a letter recently received:

> A friend in Vienna sent me the twenty-five schilling coin honoring Auer von Welsbach. So far as I know this is the first instance where a scientist has been honored in such a manner. I wonder if numismatists among your readers know of any other similar commemorative coins.

Any numismatists? Any information?—*The Editor*

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A Polymer Chemistry Course Based on Theoretical Principles

Because of the increased demand by industrial laboratories for chemists adequately trained in the principles of polymer chemistry during the years immediately following World War II, an instructional program at the graduate level was initiated in this area at the University of Florida. This increased demand is substantiated by a recent survey (*1*) which shows that about one-third of all American chemists and chemical engineers are employed in industries dealing with polymeric materials. In view of these facts, it can probably be assumed that a considerably larger portion of recent graduates are accepting positions with industries dealing mainly with polymers.

The profound interest of industrial executives in having their prospective employees obtain a general knowledge of the nature of high polymers is borne out by the fact that as early as 1950, The Society of the Plastics Industry made available a well planned brochure entitled "A Program for Plastics Education in Science and Engineering." This interest among employers has become evident in other ways; for example, premium salaries are often offered to those having such training and more rapid advancement of individuals having previous training in this area is often the case.

Students trained in such a program would be expected to fill research positions in industry. The graduate chemist would most likely find his way into the development of new high polymeric materials rather than into the manufacture of the finished products. He is likely to be assigned a problem primarily concerned with the exploration of new polymers and the development of materials to meet new requirements for a specific use. Consequently, he needs a thorough grounding in the fundamentals of high polymers and the chemistry of their formation. Another area in which there is an increasing demand for chemists and chemical engineers with fundamental training in this area is the teaching profession. While the number of colleges and universities offering formal training in this area in the past has been small, this number is increasing and adequately qualified teachers must be provided.

Due to the wide variety of interests of industrial polymer research laboratories it did not appear likely that a training program designed merely to acquaint the student with the uses and applications of a wide variety of commercial plastics and resins could be uniformly beneficial to research chemists. A program based on theoretical principles as applied to high polymers could be beneficial to all.

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Curriculum Considerations

The design of the instructional program took into consideration the following factors:

(1) Students permitted to enter into this program have a thorough background in chemistry, physics, and mathematics.

(2) They will take as prerequisite or corequisite subjects, courses in advanced organic and physical chemistry, thermodynamics, kinetics, and instrumental analysis.

(3) Lectures must be accompanied by a laboratory designed to acquaint the student with the organic and physical principles involved in monomer synthesis, polymerization, and determination of fundamental polymer properties.

(4) A research program must be available to permit interested students to apply the principles encountered in the course program to a program of research.

The prerequisite, "thorough background," allows few undergraduates to enroll. Most undergraduate chemistry and chemical engineering curricula include both organic and physical chemistry during the student's third year, preceded by one or more years of physics, mathematics through calculus, and the usual courses in general and analytical chemistry. According to these criteria, undergraduate students could qualify. However, the "distribution requirements for graduation" set up by faculties of colleges and universities often keep the average undergraduate program from including such a "highly specialized course." While members of science faculties are often inclined to discount the value of courses in the arts and humanities in favor of more scientific courses for the undergraduate, the general reaction from industry is that this trend toward a more general education is desirable.

Even though undergraduate students do not ordinarily take the course program discussed in this paper, there are ample opportunities to introduce the student to certain concepts of high polymer chemistry. Both the value of such instruction and means of accomplishing it are discussed in other papers of this symposium (*2*, *3*). In high school chemistry courses, and perhaps even more effectively in general chemistry courses in college, the impact of polymers on the life of the average person today can be used as an incentive to interest qualified students in chemistry or chemical engineering as a profession. An entire undergraduate

chemistry program could be designed in which the chemical behavior of monomers or polymers provides illustrative examples of all the principles discussed. For the chemical engineer, in addition to the above, integration of an elementary discussion of the properties of polymers into courses in mechanics, strength of materials, materials of construction, and mechanical drawing could readily be accomplished. Such an approach, however, could hardly be expected to give the embryonic polymer research chemist the thorough background which he needs.

An understanding of the mechanisms of polymerization reactions cannot be attained readily without a thorough course in organic reaction mechanisms. Such a course is not usually included in an undergraduate curriculum. The thermochemical problems of modern processes for monomer syntheses or for polymerization reactions cannot readily be understood without a more thorough treatment of thermodynamics than is usually possible in the undergraduate course in physical chemistry. The same conclusions can be drawn relative to the kinetics of polymerization, thus emphasizing the importance of a course in chemical kinetics, either as a prerequisite or corequisite for the course in polymer chemistry. Because of the wide application of instruments to the determination of the fundamental properties of polymers, as well as to the establishment of the structure and purity of monomers, a laboratory course in instrumental analysis is essential. While the student does not necessarily use such instruments as the light scattering photometer, the ultracentrifuge, and the electron microscope in such a course, his background and experience in the use of other instruments is valuable when he is required to use them.

The old theory of learning by doing dictates that such a course would not be complete without an adequately planned and guided laboratory program to accompany the lectures. While it is obviously not possible to have the student do experiments to illustrate every principle discussed in the lectures, those which are done are scheduled to follow the lecture on the same subject.

The Course Content

The course consists of 30 one-hour lectures covering the following general topics: early history of polymers, polyfunctional molecules and polymerization, catalyst systems, addition and condensation polymers, structure studies, molecular weight determinations, kinetics of polymerization, reactivity and structure of monomers and radicals, natural high polymers, properties of plastics, elastomers, and fibers, and the relationship between structure and properties.

The widely divergent ways in which the various phases of technology have developed makes it appropriate to begin with some discussion of the history of these developments. "Plastic, synthetic resin, and rubber" are all older terms than "high polymer." The relationship of these areas to the general field is discussed in the opening lecture. During the early history of the development of organic chemistry, chemists expected to obtain pure crystalline compounds, and developed a natural tendency to discard as undesirable by-products any accompanying resinous noncrystallizable product. For example, in 1872, Baeyer observed that phenols condensed with aldehydes, producing resinous or amorphous products, yet it was not until the early part of the present century that Baekeland recognized the commercial value of these products. Sir Gilbert T. Morgan made the following statement in 1939, as he regretfully recalled how he missed the critical deduction in 1893 when he was investigating the reaction of phenol with formaldehyde in a search for new dyestuff intermediates (*4*):

> A condensation product was obtained which did not do what we wanted. I set the product aside in a wide-mouth stoppered bottle, and it gradually solidified to a clear amber resin. I often think of the contents of that bottle which contained the potentialities of fortune, although we did not perceive it at the time.

The progress of high polymer chemistry has been hampered inadvertently in a number of ways. For example, a common attitude among organic chemists in which they refer to polymer preparations as "the chemistry of gunks" has tended to discourage an active interest in this field. The work of many outstanding polymer chemists has been very effective in overcoming such an attitude. They have shown that these materials obey the laws of chemistry, and the previous apparent anomalies in the behavior of polymeric materials can be explained readily in terms of theoretical principles now well understood. Another misconception which held up progress in the field of polymer chemistry revolved about the reluctance of early chemists to accept the macromolecular theory. For example, it was not until 1953 that Dr. Hermann Staudinger received the Nobel Prize for his proposal and proof of the macromolecular hypothesis made in the decade following 1920 (*5*). Previously, such outstanding colloid chemists as Ostwald, whose opinions were highly respected, maintained that virtually any substance may be obtained in the colloidal state just as it may occur under various conditions as a gas, a liquid, or a solid. It was assumed that Raoult's laws of the ideal solution did not apply to materials in the colloidal state. All structures which gave high molecular weight values were explained in terms of physical aggregates of small molecules held together through the action of intermolecular forces of mysterious origin. While both rubber chemists and cellulose chemists were reluctant to accept the macromolecular theory, protein chemists apparently had no such misconceptions. As early as 1914, Emil Fischer considered proteins to be high molecular weight polypeptides (*6*). This apparent lack of communication between protein chemists on the one hand and the rubber and cellulose chemists on the other substantiates the previous statement concerning the widely divergent nature of the development of the various phases which we now recognize as divisions of high polymer chemistry.

This historical discussion is followed by the introduction of the concept of polyfunctionality of molecules and the principles of polymerization. Included in these lectures are discussions interrelating the general concepts of organic reaction mechanisms with the reactions occurring during the polymerization processes. The chemistry of organic peroxides and other free

radical producing catalysts is included. The various methods of determining chemical and physical structure of polymers such as infrared analysis and X-ray diffraction as well as various methods of determination of absolute molecular weight values are introduced. The relation between absolute molecular weight values and intrinsic viscosity is discussed, as well as the number-average and weight-average molecular weight values. The kinetics of both condensation and addition polymerization is discussed, and the relative reactivities of the intermediate free radicals produced during vinyl type addition polymerization are used as an introduction to copolymerization and heteropolymerization.

No program in polymer chemistry would be complete without a discussion of the naturally occurring high polymers, since these have always served as working models for polymer chemists. The structures of proteins, cellulose, natural rubber, and lignin are compared with those of synthetic polymers.

The physical and chemical aspects of polymers which permit them to function as plastics, elastomers, or fibers are considered in relation to the physical requirements for these specific applications. Among the theoretical principles considered in this discussion are proton bonding, intermolecular attraction forces, crystallinity, second order transition temperatures, steric interaction, rubber elasticity, and the effect of crosslinking and branching on polymer properties. Figure 1 provides such an example by showing the effect of intermolecular forces on polymer properties. In a bundle of oriented chain-molecules, such as a synthetic textile fiber, the tensile strength is due to two principal factors—the intrinsic strength of the primary covalencies defining the chain backbone; and the resistance to mutual chain-slip offered by interchain attraction due to secondary forces, hydrogen-bonding, etc. If the mean chain length is very small, the points of interchain attachment by such forces will be relatively few, and, since they are much weaker than primary covalencies, application of stress is here likely to cause the fiber to fail by mutual chain-slip than by actual primary bond rupture. It can therefore be seen, in a qualitative way, that in order to build up the tensile strength to the point where failure can occur only by rupture of the powerful covalent bonds, the chain length must be greater than a certain minimum value (*7*).

The laboratory consists of 15 three-hour periods of experiments selected from the following: monomer synthesis; condensation polymerization; addition polymerization; copolymerization and heteropolymerization; stereospecific polymerization; crosslinking and gelation; fractionation of polymers; molecular weight determinations; correlation of intrinsic viscosity with molecular weights; and determination of polymer structure. For those students who are interested in doing additional experiments, equipment is available for determination of crystallinity of polymers by X-ray diffraction studies, electron microscope studies, and use of the ultracentrifuge.

The laboratory program is integrated with the lecture program so that a number of theoretical principles can be illustrated in a practical way. Although most students in this program have had ample experience

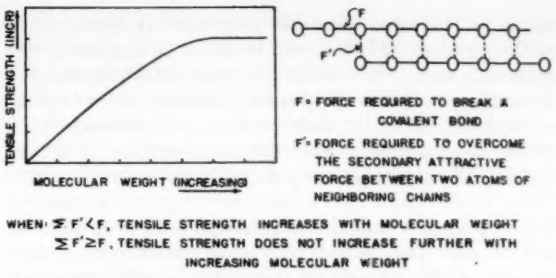
TENSILE STRENGTH (INCR)
MOLECULAR WEIGHT (INCREASING)
F
F'
F = FORCE REQUIRED TO BREAK A COVALENT BOND
F' = FORCE REQUIRED TO OVERCOME THE SECONDARY ATTRACTIVE FORCE BETWEEN TWO ATOMS OF NEIGHBORING CHAINS
WHEN: ΣF'<F, TENSILE STRENGTH INCREASES WITH MOLECULAR WEIGHT
ΣF'≥F, TENSILE STRENGTH DOES NOT INCREASE FURTHER WITH INCREASING MOLECULAR WEIGHT

Figure 1. A schematic representation of a hypothetical polymer chain and the relationship between molecular weight and tensile strength.

in preparative organic chemistry by this time, they are given the opportunity to prepare a typical vinyl monomer; for example, a substituted styrene, vinyl ether, or vinyl ester. Another experiment involves formation of a typical condensation polymer in which effect of *p*H, temperature, ratio of reactants, and other variables on the properties of the product can be observed. An unsaturated polyester is usually prepared which can also be used to illustrate the principle of functionality of such a polymer toward addition polymerization and copolymerization. Heteropolymerization is usually illustrated by use of maleic anhydride in a system employing one of the readily available olefinic monomers. By use of the aluminum trialkyl-titanium tetrachloride co-catalyst system (*8*), the principle of stereospecific polymerization is illustrated. The effect of crosslinking on the properties of a polymer is illustrated by use of divinyl benzene or other tetrafunctional diene as a crosslinking agent for a typical monomer, followed by a brief examination of the properties of the product.

In connection with the determination of molecular weight of polymers, fractionation of a typical polymer is done. These experiments, followed by intrinsic viscosity determination, permit re-emphasis of the concepts of number average molecular weight, weight average molecular weight, molecular weight distributions, intrinsic viscosity-molecular weight relationships, and the theory of the principles involved in molecular weight determinations. As an illustration of chemical means of studying the structure of polymers, a simple experiment designed to determine the relative positions of functional groups in the polymer chain is done. Infrared methods are also used in studying polymer structure.

The research program consists of preparation and polymerization of new and unusual monomers, a study of the mechanism of the organic reactions involved in monomer synthesis, the mechanism of polymerization, and the structure and properties of the polymers. A typical research problem includes three phases. The first involves the synthesis of a series of closely related monomers. Usually, these monomers will differ considerably in structure and method of preparation from commercial monomers. This phase of the problem gives the student the necessary experience in synthetic organic chemistry, since he must use the literature in search of methods of synthesis, or must devise methods of his own. This is followed by a polymerization study, which involves selection of a suitable catalyst system and set of conditions which

result in the most desirable polymer. A third phase of the problem includes a study of the properties of the polymer, and will usually include determination of infrared absorption properties, melting or softening point and solubility, fractionation, determination of molecular weights of the various fractions, and correlation of molecular weights with intrinsic viscosity. Other areas which have been investigated in the research program include preparation and properties of certain ionic polymers produced by direct polymerization, a study of certain two-stage polymerizations, and the mechanism of cyclopolymerization (*9*).

Students participating in this program are awarded degrees in either organic or physical chemistry, and are required to satisfy all of the departmental requirements for these degrees. While most have accepted positions in industrial laboratories, a number have accepted teaching positions and this number is expected to increase in the future.

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Kinetics of Polymer Formation by Free Radical Mechanism

One of the industries which has experienced a most rapid expansion since World War II is that involving the synthesis of high polymers (plastics, rubbers, and resins) from materials of low molecular weight. Along with this greatly increased industrial activity has come intensive research into the conditions under which these polymers are formed. Often in industrial laboratories the work looked toward means of improving and controlling commercial products, while in the universities there was more emphasis on the determination of constants of reaction, elucidation of mechanisms, etc. In each case the result has been a gain in insight into the nature of the polymerization process.

The majority of the vinyl polymers prepared for industrial consumption up to the present have been made by a free radical chain process. Thus this process has been thoroughly explored both theoretically and experimentally. It has been possible to learn a great deal about it and also as a result of this thorough study much has been learned about other free radical processes with small molecules.

The reaction to be discussed may be represented in a general way as:

$$n(CH_2{=}CH) \rightarrow R\text{-}(\text{-}CH_2\text{-}\underset{X}{CH}\text{-})_n R' \qquad (1)$$

Here we consider a vinyl monomer, which is an organic compound containing a double bond which is activated by a substituent X, where X may be

$$-\overset{O}{\overset{\|}{C}}-OCH_3,\ -\overset{O}{\overset{\|}{C}}-OH,\ -C{\equiv}N,\ \phi, \text{ etc.}$$

This is first converted from a low viscosity liquid to a higher viscosity liquid and finally into a glassy solid. The process is speeded up by heating, exposure to ultraviolet light or addition of organic compounds, such as peroxides and azo compounds, which are known to break down readily into free radicals.

The process is accompanied by an evolution of heat and a shrinkage of about 20% in volume. The disappearance of the double bonds can be followed easily by bromine titration during the reaction, and this affords one means of studying the kinetics of this reaction. Another possibility for rate studies is to follow the increase in refractive index as polymerization proceeds. This is also related to the change in molar refractivity due to a loss of double bonds. A method which is more widely used is to follow the change in volume as a function of time, temperature, and other experimental variables. The simplest method is to stop the reaction after various periods of time and recover the high molecular weight product by making use of the change in solubility properties on going from monomer to polymer. For example, styrene is completely miscible with methanol, while the polymer, after about the trimer stage, is very insoluble in this solvent. Thus, if a mixture of styrene and polystyrene is mixed with excess methanol the polymer is obtained as a white precipitate while the monomer dissolves in the methanol. Since it is a characteristic of free radical polymerization that high molecular polymer is formed from the beginning of the reaction, the potential loss of dimeric and trimeric material is not serious under usual conditions. The

polymer is dried and weighed and a sensitive measure of polymerization rate is obtained. The chief difficulty in this method is that it does not allow a continuous observation. Also it is not applicable to the study of the short initial period of polymerization before "steady state" conditions have been established.

The polymerization reaction shows typical chain behavior. Only a trace of free radical producer is needed to cause the reaction of a large amount of monomer or, on the other hand, only a trace of some other substances (e.g., O_2, I_2, nitro compounds, quinones, etc.) will inhibit the reaction completely. From the molecular point of view this corresponds to the situation in which one free radical initiates a reaction chain which ultimately involves several hundred monomer units before the radical activity is lost in some kind of termination reaction. The trace inhibitor then is only required to terminate this reaction chain at an early stage to prevent the reaction of several hundred monomer units and to suppress completely the macroscopic reaction.

History

High polymers have been produced for a long time. For example, polystyrene was first prepared by Simon (*1*) in 1839, and innumerable organic chemists have been bothered since then by the appearance of high molecular weight tars in otherwise attractive reactions. However, two developments were necessary before a meaningful approach to the kinetics of vinyl polymerization could be made.

In the first place it was necessary to recognize the polymeric nature of the product. Simon regarded his reaction as one of oxidation and the product as styrol oxide. Later work disproved this since no oxygen was found in the product and in fact it had the same elemental composition as the monomer itself (*2*). Berthelot (*3*) recognized by 1866 that the product was essentially the result of the coming together of the organic chemical units (monomer) to form a larger unit (polymer). It still did not seem likely to most scientists, however, that molecules of the tremendous size of high polymers could exist. They sought instead to explain the properties of polymers and of their solutions by other means of combination than the usual chemical ones which apply to low molecular weight materials.

Graham (*4*) in 1861 found that the materials which we call high polymers (both natural and synthetic) fell within the class he called colloids. They would not pass through semipermeable membranes, they diffused slowly in solution, and they had negligible effects on the freezing points of solvents in which they were dispersed.

Other members of this class were shown to differ only physically from their more common crystalline modifications. For example, the purple gold sol was only a very finely dispersed physical mixture of ordinary gold and water. Thus it was attractive to consider that the polymer materials were likewise physical aggregates of smaller, more manageable (and imaginable) organic molecules. These smaller molecules, in the case of synthetic polymers, were often supposed to be cyclic derivatives of the original monomeric structure.

This aggregation hypothesis gained support from the observation that it was often possible to recover the original monomer in yields of 50% or greater simply by heating the polymer to a high enough temperature (300°C and higher). This observation is now known to be due to another free radical chain reaction which proceeds in the direction of depropagation at the higher temperatures.

Another explanation which was advanced was based on analogy with coordination compounds. Here the idea of residual affinity or partial valency was made use of to explain the large units found by some investigators by freezing point depression (*5*) and osmotic pressure determination (*6*).

The turning point in this series of investigations came in 1920 when H. Staudinger first stated his firm belief in the linear chain form of polystyrene, polyoxymethylene, and natural rubber (*7*). This statement was followed by a long series of experiments and articles which finally established the validity of his assertion. The development of the knowledge of polymeric structures from this point on has been given previously in THIS JOURNAL (*8*).

The second necessary antecedent to the development of polymer kinetics was the development of the concept of a chain reaction. This was first suggested in 1919 independently by Christiansen, Herzfeld, and Polanyi as an explanation of the rather complicated rate expression which had been obtained experimentally by Bodenstein in 1906 for the rate of formation of HBr from H_2 and Br_2. The proposal of a chain mechanism with free radicals acting as the chain carriers in a polymerization was first made by Taylor and Jones (*9*) in 1930 in discussing the polymerization of ethylene in the gas phase under the influence of ultraviolet light and photosensitized by Hg. This followed the earlier work of Taylor (*10*) which indicated that ethylene gas could be polymerized by free radicals.

Once the possibility of having very long chain molecules was recognized and the further possibility was suggested of forming such long chains in a short space of time after an active species was produced, it was possible to proceed with a systematic study of the over-all process and its various steps.

The Mechanism of the Vinyl Chain Reaction

A number of excellent reviews of vinyl kinetics have appeared in recent years and the reader is referred to them if he desires a more detailed treatment than is useful here (*11*).

We will consider first the simple system in which pure monomer is polymerized with only an initiator present. The basic steps in the vinyl polymerization free radical chain reaction are:

First: The initiation of the chain process, by introducing a reactive free radical into the monomer.

Second: A growth period in which the free radical activity is maintained and passed along from one monomer unit to another as successive units are added to the polymer chain.[1]

Third: The termination of the free radical activity and with it the termination of the growth of the polymer chain. In the

[1] It should be noted that the vinyl chain reaction differs from that in the case of, e.g., $H_2 + Br_2 \rightarrow 2HBr$, since in the HBr case the chain carriers H· and Br· are constantly regenerated as long as the kinetic chain continues while in the polymerization case the chain carrier is the constantly growing polymer radical.

simplest case this termination occurs by the interaction of two growing polymer radicals.

Initiation

Initiation is a two-step process. The first step is the production of free radicals in the system by introducing some compound into the monomer which breaks down thermally and homolytically. A wide variety of these are available. Most commonly used are the organic peroxides (ROOR) and hydroperoxides (ROOH). These can be obtained with widely varying heat stabilities depending on the nature of the organic moiety R. From a kinetic point of view most of these compounds suffer from the fact that the production of radicals from them does not follow the simple first order dependence on peroxide concentration as might be expected for homolytic cleavage. After the concentration of radicals in the system has increased somewhat, induced chain decomposition due to attack of the initial free radicals on undissociated peroxide begins to make important contributions to the number of radicals produced. The amount of induced decomposition is dependent on the environment. Thus, in any given situation one cannot be certain what the exact rate of production of radicals from the peroxide is. Fortunately, certain members of the class of azo compounds do not show this induced decomposition. The azonitriles (especially N,N′ azobisisobutyronitrile) show clearcut first order kinetics with the same rate in a large variety of solvents. Thus, if one makes use of azobisisobutyronitrile as the initiator in a kinetic study one has eliminated one of the possible variables since the rate of radical production can be calculated for a given concentration of initiator and given temperature.

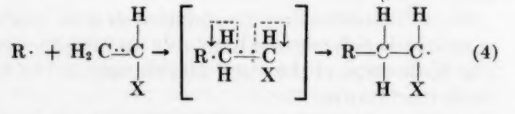
After the radicals have been produced in the system the initiation step is completed when these "initiator" radicals add to a vinyl monomer and make it into a free radical.

The over-all initiation process can be represented as:

$$\text{Init} \xrightarrow{k_d} 2\text{R}\cdot \qquad (2)$$

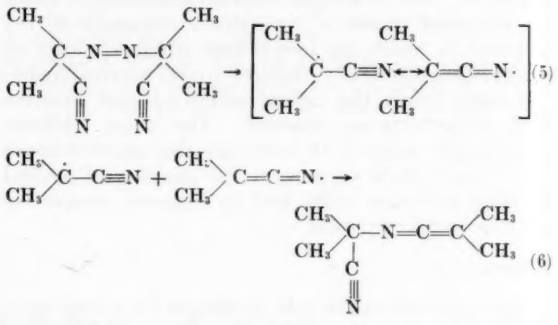
$$\text{R}\cdot + \text{M} \xrightarrow{k_i} \text{M}_1\cdot \qquad (3)$$

Here R· is the radical produced by the cleavage of the initiator, M is the monomer, and $\text{M}_1\cdot$ represents a "polymer" radical which has only one monomer unit incorporated in it. Reaction (3) may be represented more fully as



(4)

Not all of the radicals R· are effective in forming polymer radicals. When the initiator cleaves in a liquid it is subjected to the cage effect of the liquid molecules which press in upon the two radical fragments and tend to push them back together. On the average the radicals will undergo a large number of collisions before they either diffuse apart or react with the monomer in the cage wall. Thus the rate of presentation of radicals to the monomer system is not as great as the rate of cleavage of the original bond would indicate, i.e., the *efficiency* of the initiator is not unity. Other processes may contribute to lowering the efficiency also. For example the primary radicals may rearrange to more stable forms which are not as reactive toward monomer units and thus have a longer life and higher probability of reacting in some wasteful reaction. In this connection, it is interesting that Talât-Erben and Bywater (*12*) found that an unstable compound was formed during the decomposition of azobisisobutyronitrile. Determination of its structure as a ketene-imine led to the suggestion of the following series of formal reaction:



(5)

(6)

Here the primary radicals are lost at least temporarily from the polymerizing system. Reaction (6) of course is only an "on paper" reaction since the actual structure of the radical is a resonance hybrid of the two extreme forms shown.

In spite of the possibility of these interfering side reactions, the efficiency of the initiator has been found to be 0.5 to 1 in most cases of vinyl polymerization.

Propagation

Once the polymer radical has been formed by the slow process described above, it readily adds to other monomer units. For example, Bamford and Dewar (*13*) find that for the thermal reaction in styrene polymerization at 100°C a polymer molecule grows, on the average, for 1.24 seconds and during this time adds a new monomer unit every 7.5×10^{-4} seconds. Thus, the average molecule produced in the reaction will have 1650 monomer units incorporated in it. Polymer of this size will be produced within a very short time after the reaction is started.

Since this reaction proceeds so rapidly, the rate of the initiation step is the controlling one for the over-all polymerization process.

The propagation reaction may be represented:

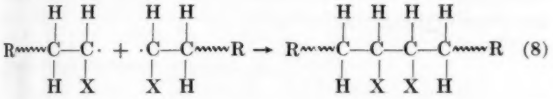
$$\begin{aligned} \text{M}_1\cdot + \text{M} &\xrightarrow{k_{p_1}} \text{M}_2\cdot \\ \text{M}_2\cdot + \text{M} &\xrightarrow{k_{p_2}} \text{M}_3\cdot \\ &\vdots \\ \text{M}_n\cdot + \text{M} &\xrightarrow{k_{pn}} \text{M}_{n+1} \end{aligned} \qquad (7)$$

It is usually assumed that the successive constants k_{p_n} are identical since they represent essentially similar reactions. This simplifies the derivation of the kinetic equations considerably. The equations derived from this assumption describe behavior of vinyl polymerization quite well provided that the reaction is not

carried too far toward completion. This assumption is not completely necessary from a mathematical point of view (*11a, 14*). Kinetic equations can be derived using more general assumptions such as that the rate constants for propagation and termination change in such a manner as to maintain the ratio k_p/k_t constant. These more elaborate approaches do not aid in explaining the experimental observations since the results are the same as with the simpler assumption.

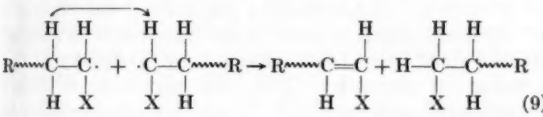
Termination

Finally, after the polymer radical has been growing for a very long time (on the time scale of ordinary radical lifetimes) it is deactivated. Most simply this involves the interaction of two polymeric radicals. Since the concentration of radicals at any time is quite low (1.8×10^{-10} M in thermal polymerization of styrene at 25°C) the probability of termination is much lower than that for propagation. (In propagation the concentration of an undiluted monomer is a little less than 10 M.) Thus the polymer molecule can become quite large before it stops growing. Termination may occur by two modes. The first, combination, is the simple coming together of two radicals so that their unpaired electrons pair to form a covalent bond.



(8)

The other possible mode, disproportionation, involves the transfer of a hydrogen atom between two radicals.



(9)

The molecular weight of the polymer will be much higher in the first case than in the second. However, in both cases it is necessary that two radicals come together. Thus the dependence of termination rate on radical concentration will be the same for both modes. In general for any given monomer it might be expected that one mode would predominate. In the case of styrene it appears that combination is the dominant, if not exclusive, termination reaction. With other monomers the situation is less clear. With all others that have been studied there appears to be contradictory evidence, some workers favoring one mode and some the other.

The termination reaction may be represented as:

$$M_n\cdot + M_m\cdot \xrightarrow{k_{tc}} M_nM_m \qquad (10)$$

$$M_n\cdot + M_m\cdot \xrightarrow{k_{td}} M_n' + M_m' \qquad (11)$$

Kinetic Equations

It is possible to derive equations which relate experimentally observable variables to rate constants for the individual steps for this simple picture.

One of the observable parameters is the rate of polymerization, R_p. This may best be defined as the rate of disappearance of monomer. From equations (3) and (7) we see that

$$R_p = \frac{-d\,[M]}{dt} = k_i[R\cdot]\,[M] + k_p\,[M\cdot]\,[M] \qquad (12)$$

Here k_p is the over-all propagation rate constant and $[M\cdot]$ is the over-all concentration of polymer radicals.

In the usual polymerization there are several hundred steps of propagation for one of initiation. The first term in (12) therefore can be neglected without excessive error. This reduces the equation to

$$R_p = k_p\,[M\cdot]\,[M] \qquad (13)$$

The concentration of radicals ($[M\cdot]$) is too small to be determined directly except by specialized techniques so it is desirable to replace this term by something more accessible. To do this, we make use of a condition which appears in many chain reactions, that is, that the concentration of the reactive intermediate species begins to come to a constant value after the reaction has gone on for a short time. The rationale of this "steady state" assumption is as follows: Initially there are no radicals in the solution. Thus the first radical produced will not be deactivated by interaction with another radical. After there are two radicals in the system there is a possibility of mutual termination but the probability is small because of the great dilution. As the concentration of radicals increases, the termination reaction becomes more likely and ultimately the rate of termination becomes equal to the rate of production of radicals. At this time the radical concentration stops increasing, and a dynamic equilibrium prevails between the initiation and termination reactions. This statement may be put into symbols as follows:

$$R_i = R_t$$

$$k_i\,[R\cdot]\,[M] = 2(k_{tc} + k_{td})\,[M\cdot]^2 \qquad (14)$$

In order to eliminate $[R\cdot]$, the concentration of initiator radicals from (14), we assume that they too come to a steady state in which their rates of production and disappearance are roughly equal. Then

$$2f\,k_d\,[\text{Init}] = k_i\,[R\cdot]\,[M] \qquad (15)$$

The factor f refers to the efficiency of initiation which has been mentioned previously and is needed in order for the equality to hold. The concentration of initiator is represented by [Init].

From (14) and (15) one obtains an expression for $M\cdot$:

$$[M\cdot] = \left[\frac{fk_d\,[\text{Init}]}{k_{tc} + k_{td}}\right]^{1/2} \qquad (16)$$

and from this, substituting in (13)

$$R_p = k_p\,[M]\left[\frac{fk_d\,[\text{Init}]}{k_{tc} + k_{td}}\right]^{1/2} \qquad (17)$$

For some purposes it is useful to note that the numerator of the fraction within the brackets is $R_{i/2}$.

Equation (17) should be compared with the relation which has been observed experimentally in many cases

$$R_p = B_I[\text{Init}]^{1/2} = K[M]^a\,[\text{Init}]^{1/2} \qquad (18)$$

where a is a number close to one but sometimes slightly greater (*15*), and B_I is a proportionality constant; a usually increases as [M] approaches zero.

No general explanation for this discrepancy between theory and practice seems to be at hand as yet.

Equation (18) holds at low temperatures where there is essentially no polymerization in the absence of initiator. At higher temperatures a thermal polymerization occurs and it has been found experimentally (*16*) that the correct expression under these conditions is:

$$R_p^2 - R_p^2{}_{,\mathrm{th}} = R_p^2{}_{,\mathrm{init}} = B I^2\,[\mathrm{Init}] \qquad (19)$$

here

R_p = the over-all observed rate of polymerization
$R_{p,\mathrm{th}}$ = the rate of thermal polymerization in the absence of initiator
$R_{p,\mathrm{init}}$ = the rate of polymerization due to initiator alone

The use of squared terms is necessary in correcting for the thermal rate since the rates of initiation (R_i) are additive for each monoradical source in the system and we see from (17) that R_i is proportional to R_p^2.

Relations of Average Molecular Weight to Kinetic Constants

In addition to the measurement of R_p for a polymerizing system it is often quite easy to measure the average degree of polymerization ($\overline{DP}$ = number of monomer units in a polymer chain) of the product polymer. This is commonly done by calibrating the dependence of dilute solution viscosity on polymer concentration in a given solvent or, somewhat more laboriously, by osmotic pressure or light scattering measurements (see e.g., ref. *11d*). Recently some doubt has been thrown on the validity of the osmotic pressure method for obtaining absolute molecular weights (*17*). The observed molecular weight appears to depend strongly on the semipermeable membrane used.

The observed molecular weights may be related to our previous kinetic discussion by noting that the ratio R_p/R_i gives the average number of monomer molecules incorporated into polymer for each effective initiating radical. This ratio is usually called the kinetic chain length (ν). The $\overline{DP}$, however, is in general not identical with ν even for this simple system. This is because of the possibility of two different termination reactions. If termination is by combination of radicals the resultant polymer will have a weight equal to the sum of the individual radical weights. On the other hand, if it is by disporportionation two polymer molecules will be formed each of which will be approximately equal in weight to one of the radicals. Thus for $\overline{DP}$ we can write the relation

$$\overline{DP} = \frac{k_p[\mathrm{M}]\,[\mathrm{M}\cdot]}{[k_{tc} + 2k_{td}]\,[\mathrm{M}\cdot]^2} = \frac{k_p[\mathrm{M}]}{[k_{tc} + 2k_{td}]\,[\mathrm{M}\cdot]} \qquad (20)$$

The comparable expression for ν is:

$$\nu = \frac{k_p[\mathrm{M}]}{2[k_{tc} + k_{td}]\,[\mathrm{M}\cdot]} \qquad (21)$$

$[\mathrm{M}\cdot]$ may be eliminated from these by use of (16). On the other hand, from (20) we can obtain the following relation:

$$\frac{1}{\overline{DP}} = \frac{k_{tc} + 2k_{td}}{k_p^2}\,\frac{R_p}{[\mathrm{M}]^2} \qquad (22)$$

by use of (13).

In this expression we see that if both R_p and $\overline{DP}$ are measured and conversion to polymer is kept low so that [M] is constant and equal to the initial monomer concentration, a measurement of a ratio of termination and propagation rate constants can be made. This ratio has been termed A' by Tobolsky, and he and his co-workers have determined its value over a wide range of temperatures for methyl methacrylate (*18*) and styrene (*19*). It is useful since (17) can be modified to

$$R_p^2 = \left(\frac{k_p^2}{2k_{tc} + 2\,k_{td}}\right)[\mathrm{M}]^2 R_i \qquad (17a)$$

The ratio of rate constants here is not identical with A' unless $k_{tc} = 0$ but it is never greater than $2A'$. Thus from the measured value R_p and the determination of A', which need only be done once for each monomer at each temperature, one can calculate the rate of initiation with an uncertainty no greater than two. In many cases the uncertainty is much less (e.g., for stryrene it is known that $k_{td} \approx 0$).

If one takes the value of a in (18) to be one, then (17*a*) is seen to be equivalent to

$$\frac{R_i}{[\mathrm{Init}]} = \frac{2(k_{tc} + k_{td})}{k_p^2}\,K^2 \qquad (17b)$$

Since $R_i/[\mathrm{Init}]$ is an expression composed of rate constants it can be presented as a function of temperature in the Arrhenius form:

$$\frac{R_i}{[\mathrm{Init}]} = Ae^{-E/RT} \qquad (23)$$

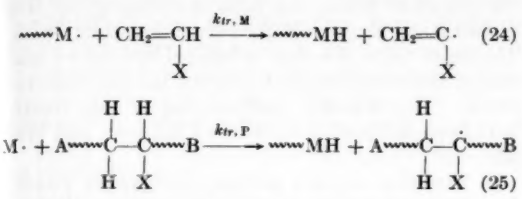
E here refers to the activation energy for initiation. This is mainly the energy for the breaking apart of the initiator into radical fragments. Thus by computing R_i at various temperatures a measure of the strength of the bond which cleaves in the initiator is available. Such values have been collected by Tobolsky for a number of peroxides (*11e*). In the case of more complicated compounds it is not always possible to say with certainty exactly what bond is breaking or the over-all process to which E refers. However, the results may sometimes be combined with other information to give insight into the reaction (*20*).

In all of these interpretations one must remember that the R_i calculated contains the previously mentioned uncertainty. Also k_{tc} and k_{td} may change in magnitude relative to each other if a wide temperature range is covered so that the relative error in R_i may not be constant.

Chain Transfer

Equation (22) implies that a plot of $1/\overline{DP}$ versus R_p will pass through the origin. In general, however, this is not the case and sometimes the line misses the origin quite badly. This situation occurs because we have oversimplified our picture of what is occurring in the polymerizing system. We have assumed that the length of the kinetic chain and the length of the material polymer radical chain are identical, that is, one initiator radical makes one and only one polymeric radical. Actually we find that it is possible to transfer the radical activity from the polymeric radical to some other species which is present. In the system we have been considering the only other species present in any

appreciable amounts are monomer and polymer. Possible reactions of these with the growing radical are:



(24)

(25)

Other atoms besides H may also be involved in such transfer steps. Chain transfer to monomer will reduce the $\overline{DP}$. The effect of transfer to polymer is to make branched instead of linear polymers, but one can see that no change in $\overline{DP}$ will result since the overall number of polymer molecules and their total weight remain the same. (This applies to number average $\overline{DP}$ only.) By including the rate expression for the transfer reaction with $M(= k_{tr,\,M}\,[M][M\cdot])$ in the denominator of (20) we can modify (22) to

$$\frac{1}{\overline{DP}} = \frac{k_{tc} + 2k_{td}}{k_p^2}\frac{R_p}{[M]^2} + \frac{k_{tr,M}}{k_p} \qquad (22a)$$

This expression fits many cases in which [Init] is low and also applies at higher concentrations of initiator for a few materials (e.g., azobisisobutyronitrile). In other cases the line becomes more and more curved as [Init] is increased. This behavior can be explained as due to transfer to initiator.

In addition it is sometimes desirable to carry out the polymerization in a solvent and transfer can occur with this to a greater or lesser extent depending on the chemical nature of the solvent. Both of these transfer reactions will change the number of polymer molecules in the system so (20) should be modified further by adding their rate expressions to its denominator. On doing this (22*b*) is obtained.

$$\frac{1}{\overline{DP}} = \frac{k_{tc} + 2k_{td}}{k_p^2}\frac{R_p}{[M]^2} + \frac{k_{tr,\,M}}{k_p} + \frac{k_{tr,\,\mathrm{Init}}}{k_p}\frac{[\mathrm{Init}]}{[M]} + \frac{k_{tr,\,\mathrm{solv}}}{k_p}\frac{[\mathrm{Solv}]}{[M]} \qquad (22b)$$

The curvature of the $1/\overline{DP}$ versus R_p plot is explained by noting from (18) that $[\mathrm{Init}] = R_p^2/B_I^2$ so that we actually have a quadratic equation in R_p.

No general expression can be written for the effect of these transfer steps on the rate of polymerization since it depends on the stabilities of the compounds and radicals involved. If one of the transfer species is readily attacked to produce radicals which are very inert toward monomer the polymerization may be completely prevented (inhibited) while this species is present. On the other hand if the transfer radicals readily attack monomer to start a new polymer chain there may be no effect on R_p. These extremes and all degrees of intermediate cases have been observed.

Absolute Rate Constants

We may note that in all the equations that we have presented thus far the rate constants for the individual steps (propagation, transfer, etc.) are never presented singly but always occur in groups as fractions. This is characteristic of all equations whose derivation is based on the steady state assumption and whose use is based on measurements of R_p and $\overline{DP}$. It seems desirable, however, not to be left with this situation but to be able to determine the values of the individual constants. In order to do this it is necessary to obtain either a value for one individual constant or a further ratio of constants which can be used with the previously determined ones to solve for the individual constants.

It should be possible to measure the steady state concentration of radicals, $[M\cdot]$, in many polymerizing systems by means of the recently developed techniques of paramagnetic resonance. If the rate of polymerization is measured simultaneously, then one can calculate the constant k_p from equation (13). Such measurements have not been carried out as yet.

A means of obtaining a further ratio of rate constants can be had if attention is directed to the periods when the system is not in a steady state. In any polymerization there is a time when the radical concentration is building up, a pre-steady state polymerization. If it is possible to remove the source of radicals suddenly, there can also be a post steady state polymerization during which the concentration of radicals and therefore R_p, gradually decreases. This may last up to several hours. Generally, the source of radicals is removed by turning off a light which has been producing them either from monomer or a photosensitizer. Either the pre- or post-effect can be studied to determine the absolute values of the rate constants.

It is also possible by use of photoinitiation to cause the rate of initiation to go through a cycle during alternate light and dark periods. If the cycle is short enough, a pseudo steady state is set up. The conditions for this pseudo steady state also give information on the kinetic constants as will be shown below.

From the previous discussion of steady state vinyl free radical kinetics we note that it is possible to define a quantity τ_s which is the average lifetime of a radical which is generated in the system. τ_s is related to ν since during τ_s there are ν monomers combined into polymers, although if transfer occurs these may be divided among several polymer molecules. In terms of symbols:

$$\frac{\tau_s R_p}{[M\cdot]} = \nu \qquad (26)$$

This can be converted into

$$\tau_s = \frac{k_p[M]}{2(k_{tc} + k_{td})R_p} \qquad (27)$$

by means of the previous equation for ν (21). Thus a simultaneous determination of τ_s and R_p will give the value of the ratio $k_p/2(k_{tc} + k_{td})$. This can be combined with our previously determined ratios, especially $k_p^2/2(k_{tc} + k_{td})$. As was noted in the discussion following equation (17*a*) there is an uncertainty here since the actual ratio determined is $k_p^2/(k_{tc} + 2k_{td})$. As before, this uncertainty is never greater than $^1/_2$ and can be negligible. For simplicity $k_{tc} + k_{td}$ will be referred to as k_t from now on.

Photo polymerization is used in a number of ways to get relations between τ_s and R_p. For example, Bamford and Dewar (*21*) polymerized a monomer by

illumination in an evacuated viscometer. The light source was then shut off and the declining rate of polymerization followed over a period of minutes or hours by observing the change in viscosity of the system. In order to do this successfully it is necessary to calibrate the viscosity changes in terms of degree of polymerization and to determine the change in degree of polymerization with rate of polymerization. It is also necessary o be able to correct the observed viscosity to correspond to the intrinsic viscosity which is obtained by extrapolating a series of viscosity measurements at various concentrations to zero concentration. If these calibrations are carried out adequately one can obtain R_p and τ_s as follows.

Under steady illumination a steady concentration of radicals [M·] will be built up. After the light is shut off this will decrease due to continuing termination with no initiation, according to the following relation:

$$-\frac{d[\mathrm{M}\cdot]}{dt} = 2k_t[\mathrm{M}\cdot]^2 \tag{28}$$

Integrating between t_0 and t gives

$$\frac{1}{[\mathrm{M}\cdot]} = \frac{1}{[\mathrm{M}\cdot]_0} - 2k_t t \tag{29}$$

Here $[\mathrm{M}\cdot]_0$ refers to the conditions under steady illumination, i.e., at steady state and t to the length of time since the light was shut off. With the help of (13) this can be converted to

$$\frac{1}{R_p} = \frac{1}{R_{p(s)}} - \frac{2k_t t}{k_p[\mathrm{M}]} \tag{30}$$

or using (27)

$$\frac{1}{R_p} = \frac{1}{R_{p(s)}} - \frac{tR_{p(s)}}{\tau_s} \tag{30a}$$

(The subscript s refers to the steady state.)

A plot of $1/R_p$ versus t should give the desired ratio k_t/k_p. This method has the advantage that the effect of small amounts of impurities in the monomer is avoided. In pre-effect studies monomer purity is much more important.

Another approach to the problem of evaluating rate constants with the aid of light is that referred to earlier in which periods of light alternate with periods of darkness. This is usually referred to as the rotating sector method since a continuous light shining through a disc with sectors cut out of it is usually used to give the alternation. In this experiment if the time of illumination is long compared to τ_s, polymerization will go on during illumination at the steady state rate. During the dark period on the other hand R_p will go to zero. Thus over a complete cycle the average R_p will be $^1/_2$ of the R_p at steady illumination if light and dark periods are equal.

On the other hand if the period of illumination is short compared to τ_s, the steady state rate will never be achieved. The most that can be said is that R_t on the average will be $^1/_2$ of R_t at steady illumination if light and dark periods are equal. Since $R_t \propto R_p^2$ this means that R_p will be $1/\sqrt{2}$ times R_p at steady illumination. If one makes a plot of the ratio between R_p (cyclic illumination) and R_p (continuous illumination) one should find that at long times of illumination the ratio will be 0.5. It will increase as the time of each cycle decreases and finally level off at very short times to a value of 0.707. Within the period in which this ratio is changing the time of illumination is of comparable magnitude with τ_s. The exact value of τ_s can be located by closer examination of the shape of the R_p versus time of illumination curve. The detailed mathematics of this treatment have been worked out by Briers, Chapman, and Walters (*22*).

A variation of (27) points out another possibility for obtaining the desired rate constants. By use of (17*a*) we can obtain the relation

$$\tau_s = \frac{1}{(2k_t R_i)^{1/2}} \tag{27a}$$

This equation, however, is not of practical utility since it is much easier to make a simultaneous determination of τ_s and R_p by methods previously described.

The direct determination of R_t is rather difficult. In the case of an initiator such as azobisisobutyronitrile the rate of production of radicals from the initiator can be calculated from the temperature and its concentration. There is still, however, the question of efficiency. How many initiator radicals actually start a polymer chain? One means of approach is to use an initiator which contains a radioactive atom (*23*). The number of these atoms combined into polymer units can be measured at low levels by the usual radioactivity techniques. This number can be compared to the total number of monomer units combined and the kinetic chain length obtained. Since $\nu = R_p/R_t$, this affords a means of obtaining R_t. To use this method it is necessary that there be no transfer to initiator and essentially no termination by initiator.

Another method of determining R_t depends on following the behavior of the initiator in the presence of varying amounts of inhibitor. The inhibitor terminates all the effective radicals produced in the system before they have time to grow into polymer. The rate of consumption of inhibitor should be proportional to the rate of initiation. There are two uncertainties here: (1) Is the efficiency of the inhibitor toward the radical the same as that of the monomer, i.e., are there side reactions of differing magnitude in the case of inhibition and in the case of polymerization? (2) How many radicals are consumed by each inhibitor? Question 2 must be answered by other indirect, and not always satisfactory, means before the calculation of R_t can be made.

Finally, (27) may be transformed again using (13) to give:

$$\tau_s = \frac{1}{2k_t[\mathrm{M}\cdot]} \tag{27b}$$

Again this is not a fruitful equation for the determination of kinetic constants because of the difficulty of determining [M·].

Readers should refer to the paper by Mayo (*24*) for rate constant data. These are given for the propagation, termination, and chain transfer steps. Comparison of these numbers will allow the reader to estimate the relative rates of the various steps in free radical polymerization.

Conclusion

A brief survey has been presented of the present state of knowledge of vinyl free radical polymerization in simple systems. The discussion has been confined mainly to bulk polymerizations in which the polymer is soluble in the monomer with a few references to systems in which a solvent is also present. These homogeneous liquids of simple composition are the easiest to study and furnish the basis for understanding the more complex cases.

Among the topics which have not been covered are inhibition, retardation, copolymerization, and heterogeneous polymerization of various sorts. These are all well covered in the general references (*11*).

At present the glamour spot in the study of polymers is that of stereospecific polymerization mentioned by McGrew (*8*). In this field, which is not closely related to the systems studied here, a big advance has recently been made and exciting developments are coming rapidly. The free radical polymer field is rather sedate in comparison and gives the appearance of only needing the finer details filled in. As in all science, however, the prediction that nothing new remains to be discovered is a dangerous one.

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Chemistry

"But what is chemistry about?" you ask.
I am struck dumb, then, robot-like, repeat,
"It is that branch of science which most treats
Of matter and its properties and its
Recombinations." The while, my mind is filled
With myriad images. I see a lone
Old alchemist intently stirring fire,
And wish that I could tell him that
His search was not all vain. He taught
Us much of properties, techniques; and we
Can make his gold, though it is dross beside
The knowledge represented, and the cost.
Berzelius sits and calculates his weights—
From crude equipment, accurate results.
John Dalton, worst experimenter yet,
Develops from wrong data bold concept.
Dissenter Priestley watches brewers' vats,
And writes about a new gas and a mouse.
Lavoisier delineates the path
For his successors—none stand tall as he.
I see a shelf of flasks more graceful than
A Grecian urn, their beauty chance result
Of chemists' need and properties of glass.
I see Grandfather's hayloft with an arc
Of light made visible by dancing chaff—
The Brownian motion and a perfect gas.
I see young Kekule's entwined snakes,
And note the glowing color in my dress.
I see the periodic chart, whole books
Of knowledge coded on a single sheet.
And there is Newton's spectrum, new refined.
Its lines bespeak of what the universe
Is made, of what, an atom; where a star
Is going; and what's in a hunk of rock.
Light. Light's the thing: the light from Bunsen flame,
The light of resonating molecules,
Electrons' motion, light behind a dial,
The glow of lonely intellect, of free
Imagination, and restless will to know.

Since chemistry's a serial story, lad,
Its brightest light lies in your starlit eyes.

Lou Bryant Kurtz
Tucson, Arizona

Paul W. Morgan
and **Stephanie L. Kwolek**
Textile Fibers Department
E. I. du Pont de Nemours & Co., Inc.
Wilmington, Delaware

The Nylon Rope Trick

Demonstration of condensation polymerization

Condensation polymers, such as the polyamides and polyesters, are usually made by tedious methods in which the reactants are melted together at 200 to 275°C with the exclusion of air. Usually some stage of the polycondensation requires high vacuum and the duration of the process may be 4 to 24 hours.

We present here a method for preparing a polyamide *instantaneously at room temperature without any apparatus* other than a drinking glass, a small jar, or a beaker. The demonstration has an air of surprise and magic about it that is intriguing to everyone from the school child to the most sophisticated chemist.

When a solution of a fast reacting diacid chloride in a water-immiscible solvent is brought into contact with an aqueous solution of an aliphatic diamine, a film of high polymer forms at once where the two solutions meet. The film is very thin but strongly coherent. The film can be pulled out of the interface and is immediately and continuously replaced to form a long, endless cord of polyamide (see Fig. 1 and cover picture). The process is like pulling a string of silk handkerchiefs out of a top hat. From clear solutions comes a cord of white polymer. When the pulling is stopped nothing appears to happen; when pulling is resumed, more polymer follows. This can be repeated over a period of many hours. The removal of film can be continued by hand or by some mechanical means at rates up to 50 feet per minute until all of one of the phases is carried away.

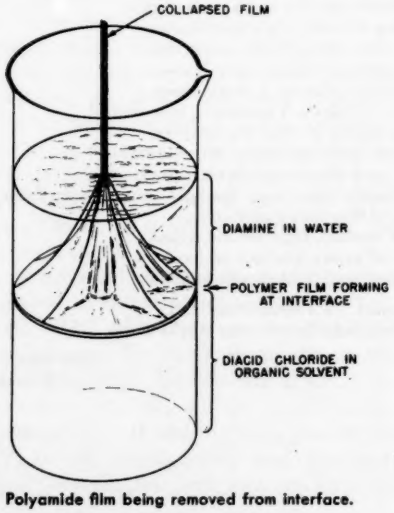
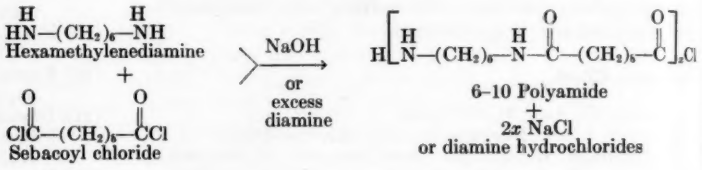


Figure 1. Polyamide film being removed from interface.

The polyamide may contain the same units as commerical nylon fiber (poly(hexamethyleneadipamide)) or it may be some homologous structure such as poly(hexamethylenesebacamide) used in nylon moldings. Even though these polyamides are formed in fractions of a second, they attain number average molecular weights of 5,000 to 20,000, which is the range for polyamides used in fibers and plastics.

The chemistry of the reaction is very simple:



The physical complexities and refinements of the polymerization method will be discussed in forthcoming publications.[1]

In the following section specific directions are given for demonstrating this fast polymerization. A wide variety of conditions and quantities will yield the desired rope of polymer. Both the volumes of the phases and the quantities of reagents may be changed considerably without causing the experiment to be inoperable. Graduated cylinders or pipets and a simple balance are sufficient for the measurement of reagents. Although a glass or beaker of almost any size can be used, one having a diameter of about two inches is recommended. In small vessels the polymer sticks to the walls, while large containers require unnecessarily large volumes of solutions.

Polycondensation Experiment

An organic phase consisting of 2 ml (0.0093 mole) sebacoyl chloride in 100 ml carbon tetrachloride (*see Safety Precautions*) is placed in a 200-ml tall-form beaker. Over this is carefully poured a solution of 4.4 g (0.038 mole) hexamethylenediamine in 50 ml water. A polymeric film forms at once at the interface. Usually it is irregular and contains air sacs and bubbles. When the film is pushed aside, new, smooth film forms at once at the

[1] The fundamentals of this type of interfacial polycondensation and the preparation of many polymers by stirred interfacial polycondensation were described by members of this Laboratory in a series of papers presented at the 134th Meeting of the American Chemical Society, Chicago, September 9, 1958, and in papers before the Polymer Section of the Gordon Conference of the A.A.A.S., New London, N. H., July 3, 1958. The method was also incorporated in U. S. Patent 2,708,617, May 17, 1955 (E. E. Magat and D. R. Strachan, assigned to E. I. du Pont de Nemours & Co.).

fresh interface. The walls of the glass are freed of strings of polymer, the mass is grasped at the center with tweezers and raised as a rope of continuously forming polymer film. The film always forms a tent having draping and shifting folds with the apex at the air-liquid interface. Dyes may be added to either phase to enhance the visibility of the liquid interface. Such an addition to the lower phase is preferable since observation of the film is obscured by coloration of the upper phase. Azobenzene is suitable for coloring the organic solvent. Phenolphthalein or common food colors may be used in the aqueous phase.

The simplest isolation method is to wash the polymer thoroughly with water and to dry it in air. The washing is greatly hastened if 50% aqueous alcohol or acetone is used for an initial wash. This treatment quickly removes the carbon tetrachloride and any unreacted acid chloride. As an alternative isolation procedure, the polymer may be dried first to remove the organic solvent and then washed well with water to remove the salts and unused reagents.

The product will have a low density and a paper-like texture which is not characteristic of the usual form of polyamides. Some may wish to show that the product is truly a polymer by further tests. One test is to show that fibers can be formed from the polymer in the molten state. First, the polymer is melted carefully on a metal spatula or spoon or in a small test tube over a hot plate or low flame; then, fibers are pulled from the melt by means of a glass rod or a match stick brought into contact with the melt and withdrawn slowly. Some discoloration of the polymer may occur from exposure to the air, but this will not affect the fiber-forming demonstration unless the polymer is charred or heated for a prolonged period. If the fibers are short or brittle, a larger amount of polymer should be used, and it should not be heated much above the temperature at which a melt is just obtained.

Another test is to prepare a film of the polymer from a solution. Many polyamides are soluble in formic acid (90 to 100%). A 10 to 20% solution of the polymer may be prepared by stirring the polymer and formic acid in a small test tube or bottle at room temperature. Heating the mixture to assist solution should be avoided, as this tends to degrade the polymer. A flexible, hazy film will form when this syrupy or viscous solution is spread on a glass plate and allowed to dry overnight in a hood. A useful device for spreading the solution may be made by smoothly winding three or four layers of cellulose tape at each end of a three-inch piece of large glass rod or a microscope slide. The number of turns of tape will determine the thickness of the film of solution and the distance between the rolls of tape will be the width of the film. One should avoid all skin contact with formic acid because it will cause deep skin burns which are not immediately obvious. If contact should occur, one should wash the exposed area thoroughly with water.

Aliphatic diacid chlorides and diamines of acceptable quality may be purchased from well-known chemical supply houses. The reagents should be kept in brown bottles having caps lined with polyethylene. The acid chlorides should be protected from humid air as much as possible. Hexamethylenediamine is sold as a 70% aqueous solution or a 97% solid and is listed as "practical" grade. This intermediate will make high quality polymer without further purification.

The aqueous solutions to be used in the experiments may be stored indefinitely. The acid chloride solutions in some solvents are not stable more than a few hours unless the solvents are purified by washing with water (as for chloform below) and/or distillation. Even solutions in pure solvents may slowly decompose after several days.

Variations of the Experiment

Poly(hexamethylenesebacamide) provides the easiest and most foolproof demonstration. The intermediates are available and easy to store. Sebacoyl chloride is more stable to hydrolysis than any of the shorter chain aliphatic diacid chlorides in contact with moist air or the aqueous phase. Sebacamides from any of the aliphatic diamines form tough films.

Other aliphatic diacid chlorides form continuously removable films with aliphatic diamines. There is a tendency for the films to be less tough when shorter chain intermediates are used. In these cases, the phases often become turbid, precipitates form away from the interface, and the continuity of film formation may be poor.

Terephthaloyl chloride forms tough film with piperazine and fair film with hexamethylenediamine when chloroform is used as the solvent for the organic phase. Film toughness does not necessarily reflect the molecular weight of the polymer in any case.

Other polyamides and other classes of condensation polymers can be made to form continuously as film. However, much greater care must be taken in selecting the solvents and reaction conditions.

In the directions given above, excess diamine was used as the acid acceptor. In order to conserve materials, one-half the diamine (2.2 g in the example) may be replaced by such bases as sodium hydroxide (1.5 g; about 15 pellets) or sodium carbonate (4.0 g). The use of inorganic bases also strengthens the polymer film. Sodium bicarbonate does not function as an acceptor in the presence of strongly basic amines. A limited excess of base will do no harm.

Preferred solvents are those with low miscibility in water and which will not react even to a low degree with the acid halide. Carbon tetrachloride functions well and is widely available in good grade. Some less toxic solvents which may be substituted for carbon tetrachloride in the given example are tetrachloroethylene, trichloroethylene, and 1,1,1-trichloroethane. The latter is reported to be the least toxic of the group. Tne concentration of acid chloride in these solvents is preferably about 3 ml per 100 ml solution. Useful nonhalogenated solvents are benzene, toluene, xylene, hexane, and cyclohexane. These solvents have a lower density than water. Therefore, when they are used, the solution of acid chloride must be placed upon the aqueous phase. The films of aliphatic polyamides prepared in these hydrocarbon solvents have a pronounced sticky quality. Film removal is often very uneven because the film sticks to the glass vessel.

Chloroform, methylene chloride, 1,2-dichloroethane, and 1,1,2-trichloroethane may be used for the reaction of hexamethylenediamine and sebacoyl chloride but a

change must be made in the concentration of the aqueous phase. The aqueous phase should be made up of 1.1 g hexamethylenediamine, 2.0 g sodium carbonate, and 50 ml water. Of these four solvents chloroform is the least satisfactory for this experiment with aliphatic polyamides. Film formation rapidly deteriorates, the phases become turbid, and the alcohol commonly used as a stabilizer in chloroform reacts with the acid chloride and reduces the molecular weight of the polymer. In order to remove the alcohol the chloroform should be washed well with water in a separatory funnel and dried and stored over a mixture of anhydrous potassium carbonate and calcium chloride.

Figure 2 shows a simple device for winding up the rope of polyamide from the interfacial polycondensation. It is useful as a means of collecting a uniform sample of polymer and permits members of a class or spectators to participate in the experiment without contact with the chemicals. Paper towels or a pan should be provided to catch any drip of solutions from the roller.

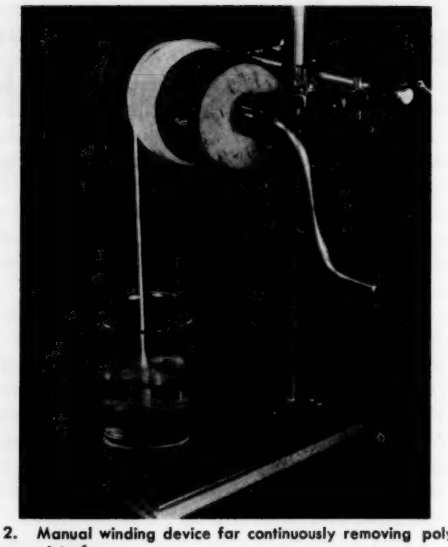


Figure 2. Manual winding device for continuously removing polyamide film from an interface.

Safety Precautions

Chemical experiments of almost any kind present some hazards. This one is relatively safe yet provides an opportunity to teach safety practice.

(1) The experiment should be carried out on a stone or otherwise solvent resistant bench top, a glass plate, or a thick pad of newspaper.

(2) Pipetting of all materials should be done with the aid of rubber bulbs and never by mouth.

(3) The work should be done in a hood or in a large or well-ventilated room. The residues should be disposed of at once or placed in a closed container. Breathing vapors of benzene, carbon tetrachloride, and chloroform, as well as skin contact with these solvents, should be avoided, since these solvents are particularly toxic and the effects can be accumulative.

(4) The use of flammable solvents, such as benzene or hexane, presents a fire hazard. No smoking, flames, or operating electrical motors and heating elements should be allowed near the experiment when these solvents are used.

(5) As much as possible, the rope of polymer film should be handled with rubber gloves, tongs, and forceps until it has been washed free of solvent and reactants. If the polymer mass is handled, the hands should be washed well with water to remove solvent and alkaline reactants.

(6) Any unused polymerization mixture should not be poured into a sink but should be stirred until no further polymer forms. The polymer mass and solvents then may be discarded with other laboratory chemicals.

(7) If acid chloride solutions are stored, they should be kept in brown bottles and out of strong light. They should be checked occasionally for operability and the presence of hydrogen chloride fumes. Decomposing solution should be discarded.

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Chemical Abstracts can use more chemically trained abstractors, especially those versed in unusual languages such as Bulgarian, Chinese, Polish, Romanian, and Russian. Abstractors with backgrounds in all subfields of chemistry are needed. Those who know petroleum chemistry and Russian are especially desired. Chemists interested in abstracting Scandinavian patents (all fields) and English, German, and French language patents in petroleum, dye, or steroid chemistry are also sought. It is not necessary that those who wish to help in the abstracting work know how to abstract at the start. *Chemical Abstracts* supplies instructions. If you are interested in this work, will you please write to The Editor, The Chemical Abstracts Service, The Ohio State University, Columbus 10, Ohio.

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Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey

Molecular Characteristics of Rubber-like Materials

Simple substances—the familiar compounds of inorganic chemistry and the simpler organic compounds—fall readily into three classes: crystalline solids, liquids, and gases. True, some substances seem not to fit into this pattern; for example, the inorganic glasses. Glasses are really only solidified liquids, however, and exceptions to the three principal states of matter are few among materials of low molecular weight.

Still, there are many substances of complex nature which fit rather poorly into this orderly scheme. Among them are many materials of biological origin—rubber, cellulose, and proteins—and also substances such as synthetic polymers. In early studies, these compounds were left out of the general classification of the states of matter, and were in fact thought to occupy some special place in the realm of solids. Part of the difficulty in understanding their nature lay, for many years, in the failure to recognize the molecular structures for what they are. For many decades it was supposed that these substances consisted of colloidal aggregations of small molecules, held together in some vague way. In the case of natural rubber, for instance, it was known a century ago that the compound is made up of isoprene, C_5H_8, but it was not until the 1920's that investigators became convinced of the giant size of rubber molecules. Many of the features of rubber elasticity were recognized quite early. For example, a century ago Joule concluded that the retractive force in stretched rubber has its origin in the thermal motions of molecules rather than in the attractive forces between molecules. The notion that high polymers are made of molecules very much bigger than those of simple compounds, and that this aspect alone is responsible for the properties which distinguish them from the clear-cut forms of matter, has been well established for only about thirty years.

The study of polymeric substances cannot be properly isolated from the study of "simple" solids, liquids, and gases. For that matter, the study of rubber-like substances properly belongs with the investigation of chain polymers in general. Compounds normally thought of as rubber-like are merely those chain polymers which have the familiar characteristics of softness and elasticity at room temperature. At other temperatures, though, similar properties are shown by quite a few substances. In fact, it is probable that nearly all chain polymers composed of very long molecules pass through a rubber-like region as we raise the temperature, provided of course that decomposition does not occur. We may relate the behavior of matter to the molecular size and to the temperature, in a purely schematic way (*1*), as is shown in Figure 1. We recall here that substances made of small molecules form crystalline solids at low temperatures and melt abruptly to form mobile liquids. With increase in molecular size, in a homologous series such as the normal paraffin hydrocarbons, the melting point rises and so does the viscosity of the liquid. The melting point does not increase indefinitely with the molecular weight but approaches a limiting value for very long molecules. The viscosity of the liquid continues to rise until the substance no longer has the familiar fluid property of liquids but instead has much of the coherence of a solid. We say then that the substance is *rubber-like*. When the molecules are small, the melting point is quite sharp. When the size is great, melting occurs over a rather broad range of temperature, and indeed the melting temperature depends to an important degree upon the rate at which the experiment is performed.

In both natural and synthetic polymers, the molecule consists of a large number of atoms, typically thousands or even tens of thousands, united by primary valence bonds (*2*). Chemically, these molecules are commonly quite simple, consisting of a characteristic group of atoms repeated over and over. Since the repeating units themselves are identical, there is no strong reason why a molecule should contain only a specific number. Rather, there is ordinarily quite a broad variation in the number of repeating units per molecule. When we speak of "molecular weight," then, we are not describing the size of each individual molecule, as we would be if we were dealing with a small molecule such as benzene. Rather, we are describing some sort of average size.

A highly important feature of linear polymers, as we now know them, is that there is great freedom of

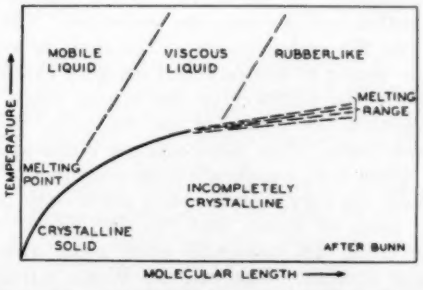

Figure 1. Variation of the physical nature of crystal-forming compounds with molecular size and temperature. After Bunn, reference (*1*).

This review is a portion of a lecture given before the Advanced Elastomer Technology Series of the New York Rubber Group, February 18, 1958.

rotation of the chain atoms about the bonds which form the chain. This flexibility differs in degree among compounds, but still it occurs universally and permits a polymer molecule to take on a large number of configurations in space. Not only are most polymer molecules flexible, but also they are in constant motion at ordinary temperatures. In some polymers the movement consists of a twisting motion of moderate amplitude, at room temperature; but in other polymers, particularly those which are rubber-like, the motions are quite violent and consist of large-amplitude displacements of chain segments.

The most obvious characteristic of the rubber-like state, and also the most important one, is the ability to undergo large elastic (i.e., reversible) deformation under comparatively small stress. The elastic extensibility is typically 1000 to 10,000 times as great as that of hard solids; and the rigidity in the region of small extensions is only $^1/_{100,000}$ that of crystalline solids. Yet rubber is strong; its tensile strength is comparable to that of cellulose and the synthetic textile fibers, and so is not too much less than that of steel.

Kinetic Theory of Rubber Elasticity

To early workers, even as late as the 1920's, the differences between rubber and the rigid solids, crystalline or glassy, had to be explained by postulating that rubber has some sort of open structure, which would allow large deformations with only small strains in the structural elements. Various configurations were proposed, spiral or liquid-like or cellular.

The now generally accepted theory of rubber elasticity was first advanced in the early 1930's by Meyer (*3*) and his colleagues, and by Karrer (*4*). Vigorous motion is typical of all molecules in the liquid state. It is a key feature of rubber-like behavior that the same sort of motion occurs in rubbery molecules. It comes about because there is great freedom for rotation about the carbon-carbon single bonds in the chain molecule. This flexibility is a common feature of all rubbers, whether natural or synthetic. It is not entirely clear why this flexibility is possessed by some substances, at a given temperature, and not by others. For example, we have only a qualitative notion as to why gutta percha should show so much less motion than its first cousin, natural rubber. Both of these substances have the same empirical formula, C_5H_8, yet at ordinary temperatures gutta percha is a rigid, partly crystalline substance, not at all resembling its isomer, rubber.

In considering the character of the motion in rubber-like substances, we should review the nature of the bonds within and between the molecules. The forces which join the carbon atoms of the chain of a rubber molecule belong to the powerful category called *chemical bonds*. In addition to the strong forces which hold together the atoms of the molecule, there are also weak forces, often called van der Waals attractive forces, which hold a molecule to its neighbors. Chemical bonds are very selective, and occur only between specific kinds of atoms, but van der Waals "bonds" are universal: all molecules exert weak attractions upon one another. The van der Waals attraction is significant only when the molecules are very close together. If we try to push the molecules still closer together, presently the orbits of electrons on one molecule interpenetrate the orbits on neighboring molecules, and the repulsions between electrons become severe. In general, the van der Waals attraction between molecules increases with the number of electrons per molecule, that is, roughly with the molecular weight.

The existence of markedly different forces within and between molecules, and the attribute of chain flexibility, combine to bring about the property of elasticity.

Since the lateral forces between chains are very much weaker than the primary valence forces along the chain direction, the thermal motions possess much greater amplitudes in the direction perpendicular to the chain than in the direction along the chain. The effect of this difference in the vigor of the motions is to tend to force the chains apart, and by the same token, to draw the ends of the chains together. That is to say, the lateral motions tend to make the chains take on disordered, contorted configurations, the obvious limit of which would be a jumbled cluster of chain segments. Notice that the picture here is strongly reminiscent of the behavior of liquid molecules, which collide with one another and assume a chaotic array in space. Indeed, the similarity between rubber and liquids is seen also in the fact that raw rubber dissolves in all proportions in suitable liquids, and that rubber can deform virtually without volume change, like the flow of a liquid. The low intermolecular forces in rubber are very much like those in simple hydrocarbon liquids.

Why is it, then, that rubber does not behave just like a liquid, with molecules moving freely past one another? Evidently, there truly is great freedom for the molecules to move past each other, but it is limited by the entanglement of the molecules—a situation which is absent in ordinary liquids. The thermal motion which brings about the liquid-like behavior in rubber also serves to keep the chains tangled. The process of vulcanization introduces chemical bonds between chains, and further reduces the freedom of flow of molecules past one another. Indeed, even in unvulcanized rubber there are occasional chemical bonds between chains, and these form a network which restricts unlimited flow.

Now, when rubber is put under tension, a restriction is imposed upon the tendency of the molecules to occupy random, chaotic configurations. That is, elongation introduces order into the array. Upon release of the tension, the thermal motions of the chain segments cause a restoration of the disordered state. In thermodynamic terms, elongation reduces the entropy. This interpretation of elasticity in terms of the order or chaos in the rubber is of fundamental importance. It sets rubber elasticity apart from the elasticity found with ordinary hard solids; for in the latter, the elastic deformation involves the stretching and restoration of bonds, that is, a change in energy rather than a change in the state of order. In fact, when rubber is deformed there is scarcely any change of intermolecular energy. This is what one might expect from the constancy of the volume: if the volume is constant, the average intermolecular distance remains unchanged, and there is no net gain or loss in the intermolecular energy.

We call this treatment of elasticity the *kinetic theory*

of elasticity, because it seeks to explain the behavior in terms of the motions of molecules, rather than in terms of their static array. We shall not go into any details of this important theory. We may remark, though, that the theory of elasticity predicts that rubber will tend to contract as the temperature is increased. This singular behavior, which is quite the opposite from the familiar expansion of ordinary material with increasing temperature, may be seen qualitatively in terms of the kinetic theory. If a sample of rubber is held in a clamp, elongated to a fixed length, the thermal motions cause the sample to tend to retract. Now, if we raise the temperature, the thermal motion grows in vigor, and the tendency to retract increases. Figure 2 shows the variation of the tension at constant

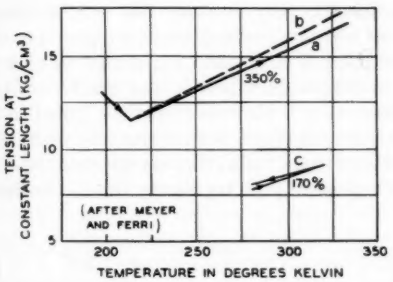

Figure 2. Temperature dependence of the tension of natural rubber elongated to constant length. (a) 350% elongation; (b) same, corrected for thermal expansion; (c) 170% elongation. After Meyer and Ferri, reference (5).

length as a function of the temperature, for two different extensions of rubber (*5*). In the upper curve, note that at low temperatures the tension decreases upon heating, over a certain temperature interval. That is to say, the substance tends to expand upon heating, just as with ordinary solids. This is the region in which the rubber is a glassy solid, rather than an elastic substance. As we shall find below, the temperature at which elastic behavior sets in has a special significance, and is called the *glass temperature*.

We should note that there is thermal expansion of the stretched rubber, along with the contraction we have just discussed. Unstretched rubber expands in the ordinary way upon heating, and elongated rubber also expands, provided the extension is no more than about 10%. At higher strains the contraction to be expected from kinetic theory of elasticity exceeds the expansion typical of ordinary solids, and so there is net contraction.

The Glass Temperature

The random thermal motion of the molecules, of which we spoke, falls off progressively at lower temperatures. When a substance has been sufficiently chilled, the thermal motion of the molecules—principally rotation of chain segments about carbon-carbon single bonds—no longer occurs at an appreciable rate. Crystallization takes place if the cooling rate is slow enough. However, with natural rubber which has been cooled rapidly, and also with substances which for structural reasons cannot readily crystallize, the loss in thermal motion leads to a change from rubberlike elasticity to glassy rigidity. The transformation is equivalent to the solidification of a liquid to a glass, as in the case of glycerol. The temperature at which change occurs is called the *glass temperature*, and also the *second-order transition temperature*.

Having identified this transformation, we must at once offer some qualifications. The term "second order transition" is used in analogy with transitions occurring in low molecular weight compounds. First, though, what is the meaning of a first-order transition? Such a transition is a change in phase which is accompanied by a discontinuity in primary thermodynamic variables, such as the volume and the heat content. Crystallization is an example of a first-order transition: it is accompanied by a latent heat and by abrupt volume changes. In addition to these first-order changes, less drastic phase changes have been observed, as in the order-disorder transformations of some alloys, and the onset of rotational motion of some small molecules in crystalline solids. These changes involve a discontinuity, not in the volume, but in the expansion coefficient; and not in the heat content, but in the heat capacity. These less drastic changes have been named second-order transitions (*6*).

The analogy between polymers and the simple compounds which show second-order transitions is not exact, however, and so the designation "glass temperature" is preferable. The difficulty occurs because in polymers we are not dealing with a true thermodynamic transition. To an important degree, the change depends upon the time scale of the experiment. In general, tests requiring shorter times tend to give higher values of the glass temperature, and often more abrupt and pronounced transformations. Conversely, in tests which are conducted very slowly there is often no evidence of an explicit glass temperature.

Values for the glass temperature have been reported for a number of compounds. Some examples are given in Table 1. These values are fairly definite, but this apparent consistency comes about mainly because most experiments occur on about the same time scale, typically several hours or a day. However, even though the glass temperature lacks thermodynamic meaning, it is still a useful quantity in the understanding of nonequilibrium behavior of material.

Table 1. Typical Glass Temperatures[a]

Polymer	T_g, °C.
Natural rubber	−73
Polyvinyl acetate	28
Cellulose nitrate	53
Polymethyl methacrylate	57–68
Polyvinyl chloride	75
Polystyrene	81

[a] Reference (*6*).

Since the glass temperature designates in an approximate way the onset of motion in the chain segments, one may anticipate qualitatively, though not quantitively, the effect of certain chemical or geometrical changes upon the glass temperature. For instance, it is well known that vulcanization introduces linkages between molecules and so tends to restrict chain motion. This restriction is pointed out in Figure 3. Here we see the glass temperature graphed as a function of quantity of combined sulfur in the vulcanizate (*6*). The more densely cross-linked the material, the greater

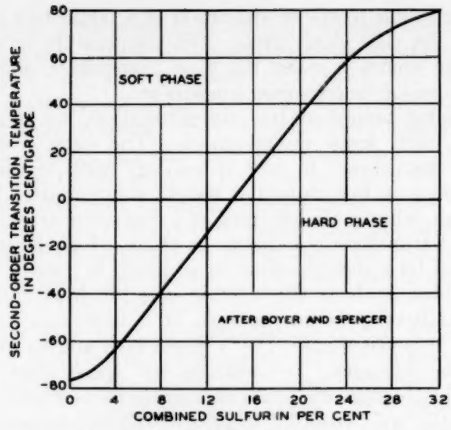

Figure 3. Second-order transition temperature in vulcanized natural rubber as a function of the amount of combined sulfur. After Boyer and Spencer, reference (6).

is the temperature which is required before thermal motion of chain segments causes a transformation from a rigid structure to the rubbery state.

The sort of transformation observed at the glass temperature is seen in Figure 4, which shows the relative volume of rubber in both the amorphous and partly crystalline states, as a function of the temperature (7). We shall have more to say about the crystalline rubber below. At a given temperature, the amorphous substance occupies the greater volume, since its chains are irregularly packed. The change in slope at about −75°C corresponds to the glass temperature. In the case of partly crystalline rubber, this change is presumed to come from the amorphous regions of the sample. Notice that at a higher temperature, about 12°C, the partly crystalline sample undergoes a further transition. Here we are dealing with melting of the crystalline regions.

The glass temperature is also seen in studies of the heat capacity. Figure 5 shows the temperature dependence of the heat capacity for amorphous rubber and for partly crystalline rubber (8). Note that the glass temperature is about −73° for the amorphous substance, and a few degrees higher for the partly crystalline. The slight shift to higher temperature in

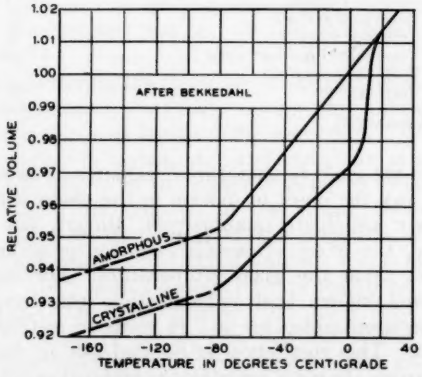

Figure 4. Temperature dependence of the relative volume of natural rubber, amorphous and partly crystalline. After Bekkedahl, reference (7).

the presence of crystallinity is perhaps due to the constraint on the motion of the amorphous segments exerted by the comparatively motion-free crystallites.

Crystallinity in Rubber

We have made passing mention of the crystalline state in rubber, though it is a fact that rubber elasticity is a feature of disordered chains. The word "crystal" implies a regularity in the external shape and form, such as occurs in substances like diamond or rock salt. A more fundamental attribute of crystals, however, is that they consist of orderly, three-dimensional arrays of molecules. Crystallinity itself has little to do with the useful behavior of rubber-like materials, except when these materials have been strained to an extreme.

Even though polymers do not exhibit the visible features of regularity which we see in quartz or diamond, many of them contain the regularity in the array of atoms or molecules which is the chief feature of the crystalline state. However, the so-called crystalline polymers are in fact semicrystalline, for there are always disordered or amorphous regions which intervene between regions of high regularity (9). The dimensions

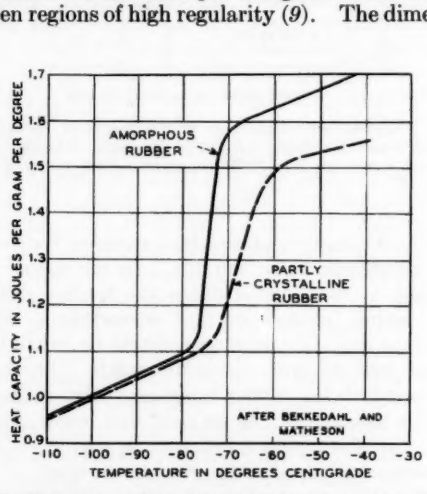

Figure 5. Temperature dependence of the heat capacity of natural rubber. After Bekkedahl and Matheson, reference (8).

of an ordered region, or crystallite as it is commonly called, are typically about 100 or 200 Ångstrom units, but the molecules themselves ordinarily have lengths which are several times greater than this. In metals there is no analogue to the amorphous regions found in semicrystalline polymers. Although most metals are polycrystalline, by proper procedures it is often possible to avoid the simultaneous formation of small crystalline regions as the substance is cooled, and instead to bring about the growth of only a single crystal rather than a polycrystalline mass. With polymers, on the other hand, the great length of the molecules makes it rather likely that a given molecule will be involved in the formation of more than one crystallite. As they grow, the crystallites compete for segments from some of the same molecules. In effect, then, there is a limit to the size of any crystalline region, since ultimately it is bound to impinge upon other crystallites with which it shares parts of the same molecules. For these reasons the crystallization

reaches a practical maximum, leaving some regions in which the chain segments remain highly disordered. It is worth noting that not only do these amorphous regions have the disordered structure reminiscent of liquids, but also they exhibit much of the agitated motion which we associate with liquids.

Some polymers, notably polyethylene, crystallize very rapidly. Indeed, it is virtually impossible to obtain them in amorphous glass-like form, even by chilling them as rapidly as possible from the melt. Other polymers, like polyethylene terephthalate and many of the polyamides, crystallize well if cooled slowly but solidify in amorphous form if chilled rapidly. Still others, such as polymethylmethacrylate and polystyrene in their familiar chemical forms, solidify without any crystallization at all.

What features of the molecular structure determine whether a polymer will crystallize quickly or slowly, or even at all? Since regularity in the three-dimensional array of the atoms is the most important feature of the crystalline state, one would expect a polymer to be able to crystallize only if its molecular structure is regular, both in shape and in chemical make-up (*10*). This view is found to be true: typical crystalline polymers are those whose molecules are both chemically and geometrically regular in structure, for example, polyethylene, the polyesters and polyamides made from straight-chain intermediates, polyvinylidene chloride, and polytetrafluoroethylene.

The typical noncrystalline polymers, on the other hand, are those in which there are chemical or geometrical irregularities. Among polymers made from two or more kinds of ingredients (copolymers), there are many in which the ingredients are quite different from each other. For example, there are the butadiene-styrene copolymers which are used as synthetic rubbers, and which cannot be made to crystallize. In polymers whose building units are all alike, noncrystallinity often results when the repeating units contain large side groups which are likely to be situated indiscriminately in left- and right-hand positions along the chain. This situation occurs when a chain carbon atom carries two different substituent groups, as in polystyrene, for example. In this polymer, the bulky phenyl group projects laterally from the chain, and ordinarily occurs randomly to the left and to the right, so that the resulting structure is irregular in form. Mere bigness of side groups, however, is not enough to prevent crystallinity. Quite recently there has been a chemical revolution in the field of synthetic polymers: new kinds of catalysts allow us to produce polymers in which most building units enter in either a left-hand or else a right-hand fashion (*11*). These synthetic materials have been named *isotactic* polymers, the word "isotactic" implying that the structural units touch each other in the same fashion. Polystyrene is an example of a polymer which can be made in isotactic form and which then possesses enough regularity of structure to crystallize.

The growth of crystalline regions, from very small clusters into larger crystallites, clearly depends upon molecular motion. It is not surprising, then, that crystallization is strongly temperature-dependent. Some of the earliest information on crystallization in polymers comes from the notable studies by Wood and

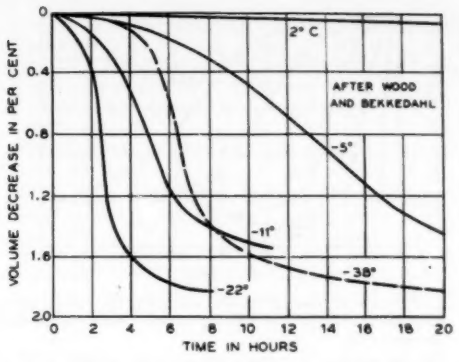

Figure 6. Change in volume of natural rubber as a function of time, for various temperatures of crystallization. After Wood and Bekkedahl, reference (12).

Bekkedahl (*12*). When rubber freezes there is a decrease in volume, just as there is with most substances. Figure 6 shows change in volume as a function of time for rubber brought from room temperature to various other temperatures. It is seen that when the temperature drop is small there is only a slight contraction over a long time interval, corresponding to the slow development of only a minor amount of crystallinity. But at lower temperatures, for example $-11°$ and $-22°$ in Figure 6, the contraction occurs progressively more rapidly and more extensively. Finally, at a still lower temperature, $-38°$, the process becomes more sluggish.

We may measure the rate of crystallization in a number of ways. For their studies of rubber, Wood and Bekkedahl measured the time for one-half of the total volume change to occur, this quantity being easier to determine than the time needed for the volume change to become complete. The reciprocal of this half-time is a measure of the average rate of crystallization in the first half of the process. Figure 7 shows the variation of this rate with temperature. It can be seen that crystallization takes place most rapidly at about $-25°$. For other polymers and for other methods of measuring the rate, one obtains curves which resemble that of Figure 7, though the temperature spread and the temperature of maximum rate may differ rather broadly.

We may interpret a curve such as that in Figure 7 in terms of molecular motion. When the temperature is comparatively high there is considerable molecular

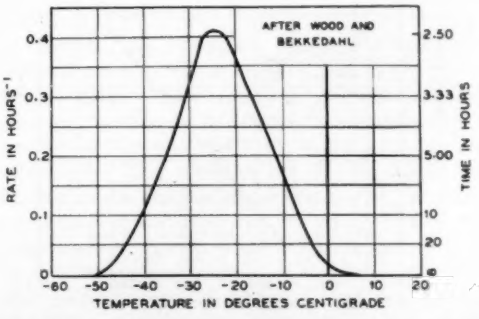

Figure 7. Rate of crystallization in natural rubber as a function of the temperature. After Wood and Bekkedahl, reference (12).

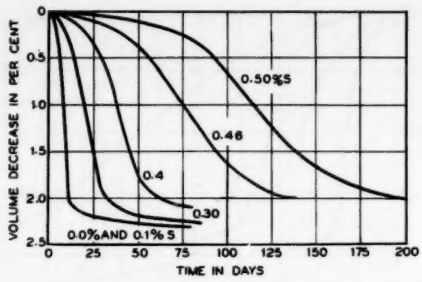

Figure 8. Variation of volume change with time, for vulcanized natural rubber containing various amounts of sulfur. After Bekkedahl and Wood, reference (13).

mobility, and hence in principle it is rather easy to move the chain segments into positions where they can become part of the crystalline lattice. But by the same token the thermal motion which aides mobility tends to disrupt orderly arrangements. In particular, the thermal agitation makes it hard for clusters ("nuclei") to form. To overcome this agitation, cooperation is needed between the attractive forces of a larger number of molecular segments than if the temperature were lower. As the temperature is decreased it becomes easier to form such clusters. The thermal motions which disrupt the regular arrays are diminished, but at the same time the chain segments retain enough mobility that they can move into more orderly configurations. At still lower temperatures, however, the chain mobility falls off to such an extent that the growth of crystallites is retarded, even though at these lower temperatures it is easy to form clusters of chain segments which will be stable.

The importance of chain mobility to the crystallization process is emphasized by a study of the effect of vulcanization upon the rate of crystallization. It is well known that vulcanization introduces linkages between chains, and so reduces the freedom of movement possessed by the rubber molecule. Figure 8 compares the time dependence of the volume change due to crystallization, for vulcanizates containing varying amounts of sulfur (*13*). It is seen that the greater the extent of vulcanization i.e., the greater the restriction upon chain mobility, the more sluggish is the crystallization process.

The crystallization which we have discussed so far has been that produced by the freezing of unstretched polymers. It is also true that crystallization is aided by elongation. Crystallization by stretching is not fundamentally different from crystallization by freezing. It occurs much more rapidly under stretching, however, and the resulting crystallites tend to be oriented in the direction of elongation, instead of being oriented at random, as they are in rubber which has been frozen without stress.

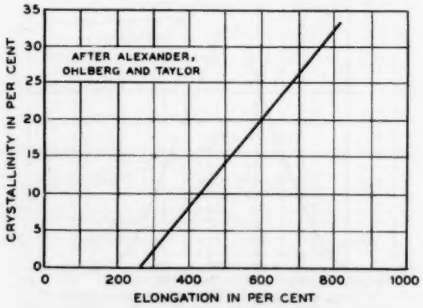

Figure 9. Dependence of degree of crystallinity upon the elongation of natural rubber. After Alexander, Ohlberg, and Taylor, reference (14).

We can see why stretching brings about crystallization if we recall that the elastic nature of rubber stems from the violent motion of the chain segments, which has the effect of forcing the chains apart and tending to draw the ends of the chains together. Now, if we apply a force which tends to elongate the chains, we oppose the disordering influences. Therefore, appreciable portions of the chains are able to pack neatly together, and we obtain the three-dimensional regularity characteristic of the crystalline state. Figure 9 shows how the extent of crystallinity varies with the elongation (*14*). As we would expect, the greater the elongation, the greater is the proportion of the material in the ordered state.

Elongation not only affects the extent of crystallinity, but also the rate of crystallization. Figure 10 shows the development of crystallinity, measured by the change in density, for unvulcanized natural rubber which had been stretched quickly at 0°C to various extensions, and kept at that temperature until crystallization was finished (*15*). It is seen that crystallinity develops much more rapidly as the initial elongation is increased.

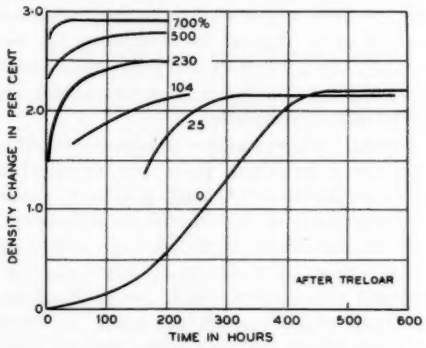

Figure 10. Variation of the degree of crystallinity, as shown by the density change, as a function of time following elongation to various extents. After Treloar, reference (15).

Crystallinity itself has little to do with the useful elastic behavior of rubber-like materials, but it becomes important to the mechanical properties of the substance when the specimen has been stretched to an extreme. We have already remarked that unvulcanized rubber is prevented from flowing like a liquid owing to the presence of entanglements between the molecules and also to the restraint of occasional bonds between chains. At low elongations these cohesive effects suffice to prevent plastic deformation. At higher stresses, when these coupling mechanisms are not enough by themselves to prevent considerable slippage, crystallization provides the necessary resistance to flow. Since the amount of crystallization increases with the stress, the resistance to increased deformation is automatically developed. Much of the heat developed on stretching rubber comes from the latent heat of crystallization.

Conclusion

We have touched here mainly on the properties and behavior of natural rubber unmodified by vulcanization or by the addition of ingredients such as carbon black. It is true that these modifications are vital to the satisfactory use of rubber-like materials for practical purposes. For example, the synthetic rubber GR-S undergoes a tenfold increase in tensile strength upon the addition of considerable amounts of carbon black, and indeed would be useless without the addition of carbon. The details of vulcanization and reinforcement of rubbers are only partly understood, and we shall not try to go into the matter here. However, the rubber-like behavior of these modified materials is based on the considerations which we have reviewed here. It is an important conclusion, from all which we have said, that rubbers and the rubber-like state are not to be thought of as distinct from familiar crystals, liquids, and gases.

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The Dissociation Constant of Iodic Acid

Experiments for the analytical laboratory

Equilibrium constants not directly related to solubility processes are nevertheless frequently determined through the interpretation of the dependence of solubility upon the presence of other substances. For example, the effect of chloride ion on the solubility of silver chloride was interpreted by Jonte and Martin (*1*) in a way which allowed calculation of the dissociation constants of $AgCl_2^-$ and AgCl. The dissociation constant of silver acetate has been determined through the effect of acetate ion on the solubility of silver bromate (*2*), and Sandell and Neumayer (*3*) were able to calculate the acid-base equilibrium constants of *p*-diethylaminobenzylidenerhodanine because of the effect of *p*H on the solubility of this compound.

These three cases are a random selection from many interesting examples in the fruitful field of indirect uses of solubility measurements. It seems worthwhile to include at least one such experiment in the undergraduate curriculum, particularly in the quantitative analysis course. An earlier paper (*4*) discussed a student experiment of this sort, namely the determination of the dissociation constant of the bisulfate ion through the effect of acidity on the solubility of lead sulfate. The experiment had the pedagogical virtues of instructing the student with respect both to fundamental and practical aspects of solubility and acid-base equilibria, of showing the technique and particular advantages of iodometric analysis, and of replacing a mere routine determination of an "unknown" with purposeful small-scale research. The response to and results of these virtues were truly encouraging, but the experiment suffered in students' hands from the necessity for very careful work if good results were to be obtained. This problem was due chiefly to the low solubility of lead sulfate, which meant that a reasonably sized aliquot of the saturated solution did not contain enough lead to permit even very small losses in the chromate separation.

The present paper describes a replacement for the lead sulfate experiment. The virtues are preserved, even enhanced, while the experimental problems are

reduced to a level easily handled by sophomores. The design of the new experiment was stimulated by the appearance of a recent paper by Peterson (*5*), which describes the student determination of the solubility product constant for copper iodate, using iodometric analysis of the saturated solutions. The higher solubility of copper iodate, coupled with the simplicity of direct titration of the saturated solution without separation and the exceptionally favorable analytical factor (13 atoms of iodine for each molecule of copper iodate) is the reason for the lack of experimental difficulty compared to the lead sulfate case.

The number of supposedly strong electrolytes has decreased so alarmingly in recent years (*6*, *7*, *8*) that one should hesitate to be casual in professing complete dissociation. However, under the conditions of this experiment the concentrations of $Cu(IO_3)_2$ ("molecules") and $CuIO_3^+$ (ion pairs) seem to be negligibly small. Also, sodium and iodate ions do not seem to associate strongly (*9*). Therefore it is proposed that the primary solubility process is:

$$Cu(IO_3)_2\ (s) \leftrightharpoons Cu^{++} + 2IO_3^-$$

Since the iodate ion has weakly basic properties, the reaction,

$$IO_3^- + H_3O^+ \leftrightharpoons HIO_3 + H_2O$$

occurs to an extent determined by the acidity of the solution. If the solubility, S, of copper iodate is defined as the molarity of copper ion in the saturated solution, the presence of two iodate ions (some of which are present as iodic acid molecules) for each copper means that:

$$S = [Cu^{++}] = {}^1/_2([IO_3^-] + [HIO_3])$$

where the brackets indicate molarities. The molarity of HIO_3 may be replaced by the quantity

$$[H_3O^+]\,[IO_3^-]/K_a$$

where K_a is the dissociation constant for iodic acid, while $[IO_3^-]$ may be replaced by $(K_{sp}/[Cu^{++}])^{1/2}$, where K_{sp} is the solubility product constant for copper iodate. Rearrangement of the resulting equation yields:

$$2S^{3/2} = K_{sp}{}^{1/2} + [H_3O^+]\frac{K_{sp}{}^{1/2}}{K_a}$$

It is explained to the student that this is a linear equation if one chooses the right variables, and that he may interpret his experimental data on the solubility of copper iodate in solutions of varying acidity by a graphical method, plotting his experimentally determined values of the quantity $2S^{3/2}$ versus his controlled values of $[H_3O^+]$. The equation predicts that the dissociation constant, K_a, can be calculated simply by dividing the intercept of the straight line by its slope. Students are often taught mathematics in a rather abstract fashion, and this sort of treatment of their own experimental data gives worthwhile insight into the practical nature of linear equations.

The Experiment

The experiment is set up and carried out as follows: Solid copper iodate is prepared as described by Peterson, although substitution of iodic acid for the potassium iodate offers the minor advantage that completeness of washing can be tested with an acid-base indicator. Also, it is desirable to sediment two or three times to remove the smallest particles, which may have an appreciably higher solubility. The instructor prepares a series of bottles containing perchloric acid and either sodium or lithium (vide infra) perchlorate, with the acid concentration ranging from 0.01 to 1.0 *M* and the inert salt molarity adjusted to provide constant ionic strength. Excess solid copper iodate (about 10 g for each liter of solution is sufficient) is added to each, and mechanical stirring for two or three days serves to equilibrate the solutions. The simple device of inserting a motor-driven stirring shaft through a cork stopper allows this to be done in a bottle kept at a fairly constant temperature. On the day for the class work the excess copper iodate is removed by filtration and the saturated solutions are placed at the disposal of the students (not without dire threats concerning contamination!). Each student pipets a 5-ml portion of each solution, adds 20 ml of water, 2 g of potassium iodide dissolved in a little water, 10 ml of 1 *M* hydrochloric acid, and then titrates with previously standardized 0.02 *M* sodium thiosulfate using starch indicator. Titration volumes will range from 20 to 40 ml. The laboratory period need not be unduly long, even if duplicate determinations are made. If the size of the class is such that the total volumes of equilibrated solutions will not be unwieldy, the instructor may prefer to have the students take aliquots of 25 ml, using 0.1 *M* thiosulfate for titration. This allows sharper end points and decreases any error associated with instability of dilute thiosulfate solutions. However, this has not been a source of difficulty in the author's experience.

The first time this experiment was tried, sodium perchlorate was chosen as the inert salt because it is cheaper than the lithium compound. The results were similar to those shown in Table 1 and by curve 1 of Figure 1. The curvature is probably due to specific effects on activity coefficients when sodium ion is replaced by hydrogen ion in the series of solutions. This curvature does not spoil the experiment. It might even be considered a good feature because it illustrates the common phenomenon of specific effects, a topic deserving of more recognition. Although it is not reasonable to take the slope of the curve as a whole, it is very instructive to point out that the value of the dissociation constant of iodic acid *in 1M sodium perchlorate* may be calculated by dividing the intercept by the *limiting* slope at that point. Again, the student has the opportunity to learn something about practical mathematics which probably was not covered in his formal course.

NOTE ADDED IN PROOF: The starch-iodine color returns not long after the end point has been reached. Although this is partly due to air oxidation of iodide in the acid solution, we have established that this is not the only factor. A possible explanation is the catalytic reduction of perchlorate ion by the copper(I) formed when excess iodide is added. Perchlorate may oxidize copper(I) to copper(II), which is re-reduced by the excess iodide. We find a permanent end point when the copper is kept in the (II) state by citrate complexing (following the directions of KOLTHOFF *et al.*, "Volumetric Analysis," Vol. 3, p. 357). Therefore, the solubilities reported in this paper are slightly high, and the experiment may be improved both from a scientific and an instructional point of view by using the citrate method.

Nevertheless, straight lines are so aesthetically satisfying that it may be preferable to avoid the curvature. One would expect the specific effects to be less apparent at lower ionic strengths. However, the dissociation constant of iodic acid is large enough to require that the acidity range up to at least about 0.2 *M*. Otherwise the solubility of copper iodate will not vary significantly.

Another approach to obtain linearity is based on the similarity of hydronium ion and lithium ion. For example, in 1 *M* mixtures of alkali metal chlorides and hydrochloric acid the mean activity coefficient of the latter is independent of the composition of the mixture only if the other cation is lithium (*10*). With sodium or potassium, specific effects on the mean activity coefficient are marked. This suggested that the use of lithium perchlorate instead of sodium perchlorate might

Table 1. Molar Solubility of Copper Iodate as a Function of Acidity

M_{HClO_4}	M_{salt}	S, when salt is $NaClO_4$	S, when salt is $LiClO_4$	$2S^{3/2}$ for $NaClO_4$	$2S^{3/2}$ for $LiClO_4$
0.010	0.990	0.00649	$5.80 \cdot 10^{-3}$	$1.05 \cdot 10^{-3}$	$0.883 \cdot 10^{-3}$
0.300	0.700	0.00872	7.99	1.63	1.43
0.700	0.300	0.0110	$1.06 \cdot 10^{-2}$	2.30	2.17
1.000	0.000	0.0122	1.23	2.75	2.72

For the lithium system: $K_{sp} = 7.6 \times 10^{-7}$
$K_a = 0.470$

give results as anticipated by consideration of the ostensibly linear equation. That the hope is fulfilled is shown in Table 1 and by curve 2 of Figure 1.

It might be of interest to let one class do the experiment with sodium perchlorate, the next class trying lithium perchlorate in full awareness of the curvature obtained by their predecessors. Another possibility is to let successive classes use different ionic strengths, so that each effort will be part of a larger plan, perhaps with the goal of eventually extrapolating the values to zero ionic strength to obtain the thermodynamic constants. Again, it may be worthwhile to replace copper iodate with some other iodate, to see whether the same dissociation constant is obtained for iodic acid. Silver iodate (*11*) and barium iodate (*12*) have been used for this purpose, but these substances are not soluble enough for sophomores. Good possibilities are calcium and cadmium iodates, the solubilities of which are higher.

By the time the student has made his analyses and calculations, prepared and interpreted his graph, and written a brief report, he has learned a good deal of theoretical and practical chemistry more richly than has been traditional in quantitative analysis. Yet the laboratory time has not been increased. It is not surprising each year to find a few students who are so interested in this way of studying analytical chemistry that they seek to do further related work on their own time. The author has heard the opinion that this approach is "too physical," but it surely is obsolescent to neatly classify good chemistry into the four historical divisions. Furthermore, analytical courses have long

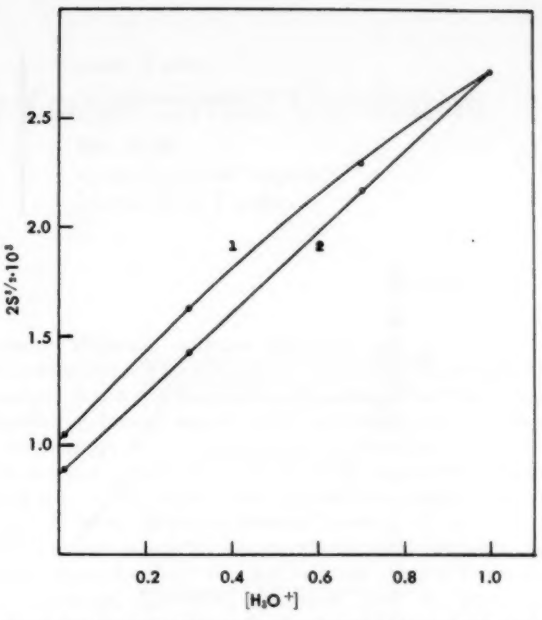

Figure 1. Graphical interpretation of solubility of copper iodate as a function of acidity. Curve 1, $NaClO_4$–$HClO_4$ mixtures; curve 2, $LiClO_4$–$HClO_4$ mixtures. Data of J. Sudmeier.

taught equilibrium theory, and what is worth discussing in lecture is certainly worth reinforcing in the laboratory. The analytical methods learned simultaneously are as meaningful as ever, and perhaps more so because they are seen in realistic perspective with their *raison d'etre* clearly illustrated.

Acknowledgment

The author is grateful to James Sudmeier for his enthusiasm and careful work in following up his class experiment with the studies involving lithium perchlorate.

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✦ ✦ ✦

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A Portable Semimicro Reaction Assembly

The portable reaction assembly shown in Figure 1 is much more compact than the permanently assembled form previously developed (*1*), but it retains most of the versatility of the larger assembly. Since all parts pack into a containing box of approximate closed dimensions 15 in. × 14 in. × 2¾ in., a dozen or more of these sets occupy very little space. An end panel, which is stored beneath assembly panel *C*, may be attached transversely to the left-hand end of *C* by means of a single thumbscrew. A rigid, self-supporting assembly is thus obtained. Although mounted in polythene-coated spring clips[1] which are screwed to the assembly panel as shown, the three-necked general-purpose flask and the distillation assembly may be at once removed and replaced by other apparatus. The latter is stored in the lift-out tray *D*, in the 1⅜-in. deep space *E* below the tray and in compartments *F*, and *G*. The lift-out wood block *H* is suitably drilled to accommodate such items as crystallizing tubes, filtration assemblies, etc., (*1*, *2*) when these are in use.

Although the end panel is wide at the bottom to give ample stability, its upper part is narrowed so that the front edge projects some 5 mm only from the face of the assembly panel. This allows overhanging assemblies to be used. Almost reaching the underside of the lid when the box is closed, a wooden pin projects from the face of the assembly panel and thus prevents it from rising during transportation.[2]

Both panels are of ⅜-in. thick plywood and are given several coats of hard-surfaced lead-free white or cream paint. The design could be adapted for molding in a suitable plastic.

The parts listed in the table are adequate for most purposes and are easily accommodated in the storage spaces provided. Heavy borosilicate glass is used throughout and in most cases each half-joint (standard taper 10/30 or British B.10) has a single glass hook. A rubber band stretched between a pair of hooks effectively prevents receivers, flasks, etc., from falling when an assembly is being handled (*3*). The three-necked flask has a large central opening and is designed for easy cleaning.

Convenient miniature accessories are: an electric stirrer equipped with a male cone, which may be inserted directly into the mouth of a flask or the top of a condenser (*4*) and a line-operated hotplate which allows sensitive control of heating (*5*).

[1] A. Gallenkamp and Co., Ltd., 19 Sun St., London, E.C. 2, England.

[2] A commercial version is now available from Aimer Products, Ltd., Rochester Place, London N.W. 1, England.

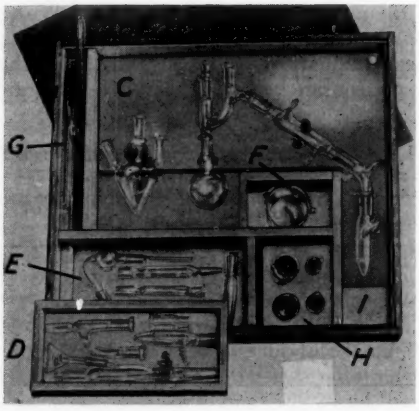

Figure 1. Portable semimicro reaction assembly in dismantled form.

Standard Set of Apparatus

Part No.	Part	Location[a]
1	Reflux-and-distil head (*2*)	*C*
2	Reflux-and-addition head	*D*
3	Water condenser	*C*
4	Distillation attachment	*C*
5	"Nail" filter	*D*
6	Filtration receiver	*D*
7	R.b. flask	*C*
8	Tap funnel	*D*
9	Receiver	*C*
10	Desiccant tube	*E*
11	Three-necked flask	*C*
12	Adaptor	*E*
13	Gas delivery tube	*E*
14	Thermometer adaptor	*D*
15	Stopper	*D*
16	Air condenser	*G*
17	Microfilter	*E*
18	Eared beaker (*1*)	*F*
19	50 × 15 mm crystallizing tube	*H*
20	50 × 25 mm crystallizing tube	*H*
21	Teat pipet (*2*)	*G*
22	Micro pestle and mortar (*6*)	*E* and *H*
23	Spring clamp (*1*)	*G*
24	6-in. thermometer	*G*
25	Stirring rod	*D*
26	Rubber tubing with adaptors for faucet	*I*

[a] The lettering corresponds with that used in Figure 1 (*C* is "on panel").

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(3) Stock, J. T., and Fill, M. A., *Chem. Age (London)*, **71**, 933 (1954).
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(5) *Ibid.*, **5**, 344 (1956).
(6) Stock, J. T., and Fill. M. A., *Metallurgia*, **38**, 118 (1948).

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Laboratory Countercurrent Distribution Apparatus

The countercurrent distribution technique developed by Craig and co-workers[1] has found considerable use in the separation and purification of mixtures. The glassblowing and mechanical requirements for building an apparatus of this type, however, often preclude its use by small laboratories.

The apparatus described here is simple to build and use. The mechanical support can be built from laboratory clamps and metal rods. The glass equilibration tubes can be made by a competent amateur glassblower.

The equilibrating and receiving tubes are shown in Figure 1. Equilibrating tube *A* is made from ordinary Pyrex tubing of a size determined by the phase volume

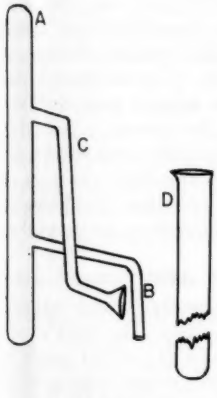

Figure 1. Equilibrating and receiving tubes.

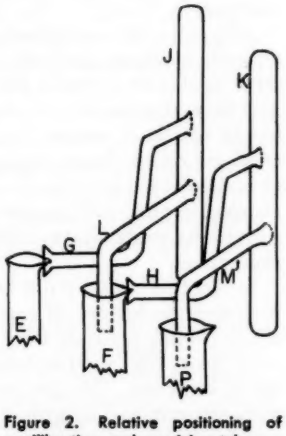

Figure 2. Relative positioning of equilibrating and receiving tubes.

requirements of contemplated distribution experiments. (In this laboratory, equilibrating tubes were made from 20-mm Pyrex tubing and contained 15 ml up to sidearm *B*. Sidearms *B* and *C* were made from 7-mm tubing, and side-arm *C* was flared out at the lower end to a width of 16 mm.) Receiving tube *D* is an ordinary test tube with a small pouring spout.

The relative positioning of the equilibrating and receiving tubes is shown in Figure 2. Receiving tubes *E* and *F* are arranged so that their spouts fit into tubes *G* and H of the equilibrating tubes *J* and *K*. Tubes *L* and *M* empty into receiving tubes *F* and *P*. This is extended to any desired number of tubes.

The mechanical framework for the tubes is shown in Figure 3. Two ring-stands form the support, and aluminum rods *a* and *b* brace them rigidly together. Rod *c* is supported by two Fisher Flexaframe clamps attached to the ring-stand rods. *c* swivels freely and

[1] Craig, L. C., *J. Biol. Chem.*, **161**, 321 (1945); Craig, L. C., and Post, O., *Anal. Chem.*, **21**, 500 (1949).

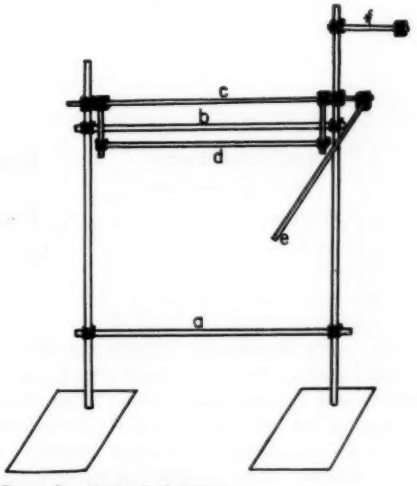

Figure 3. Mechanical support.

has a handle, *e*, tightly clamped at the end. Rod *d* is supported parallel to *c* and at a distance of about four inches from it by laboratory clamps and short rods. Handle *e* can be held in the vertical position by rod *f*, which is clamped to the ring-stand rod. *f* is clamped only semi-rigidly so that it can be moved back and forth, depending on whether or not it is desired to restrain handle *e*.

The glass tubes are attached to rods *c* and *d* in one of two ways. If the number of tubes is small, they may simply be supported by laboratory clamps. For a large number of tubes, however, the support shown in Figure 4 is better. Two such supports are needed; one holding the receiving tubes and attaching to rod *d* of Figure 3, the other holding the equilibrating tubes and attaching to rod *c*, Figure 3. Two pieces of wood form the tube holder *g*. One of these is notched and the other is flat, with a rubber strip nailed onto the inner face to insure that the glass tubes are gripped firmly. The wooden pieces are held together with bolts and wing-nuts *h*. Rods *j* attach to the back of one of the wooden pieces of the tube holder by means of laboratory feet or flanges.

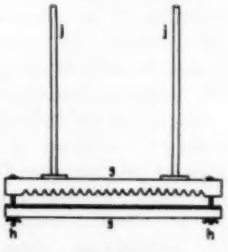

Figure 4. Tube support.

The apparatus is used in the manner described by Pinsky,[2] so that with the present design it is unnecessary to shift the receiving tubes to the right or left between equilibrations. Raising handle *e* (Fig. 3) to the

[2] Pinsky, Alex, *Anal. Chem.*, **27**, 2019 (1955).

vertical position causes the contents of the receiving tubes to flow into adjacent equilibrating tubes. Lowering *e* causes lighter phases in the equilibrating tubes to flow into the respective receiving tubes.

The suggestion by Pinsky that each equilibrating tube be made with a standard taper cap large enough to contain the entire contents of the tube can be followed where emulsification is likely to occur. Individual tubes can be removed for centrifuging if necessary. The framework and supporting clamps can be assembled without access to a machine shop. There is no need to shift the relative position of receiving and equilibrating tubes during an entire run. Individual receiving and equilibrating tubes may be removed and replaced at any time during the run. Flow of the lighter phase from equilibrating tubes is smooth and free from bubbling, due to the fact that these tubes have two side-arms, the upper one allowing passage of air in as liquid flows out of the lower one.

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Friedrich Goppelsroeder, Pioneer of Paper Chromatography

The beginnings of paper partition chromatography stem from the experiments of Runge, Schoenbein, and Goppelsroeder, who studied capillary analysis during the last half of the nineteenth century. The technique of capillary analysis resembles paper chromatography; a strip of filter paper is dipped into a solution of a dye or salt and the extent of rise of the liquid is noted as well as the appearance of the material under investigation. Zones appear colored or may be detected by some specific reagent.

Of the three men mentioned above, Friederich Goppelsroeder (1837–1919) devoted his career to experiments involving capillary analysis. He was a student of Schoenbein's and began working in this field in 1861. Although his work must be judged crude by present standards he suggested a number of techniques which are in current vogue.

Goppelsroeder was able to separate mixtures of dyes and to determine the components of pure dyes by this method. Thus, he was able to separate picric acid from curcuruma dye and from indigo.[1] He showed that commercial fuchsin contained one more component than did pure fuchsin. When textile merchants complained that azulene dyes gave a purplish cast to their material Goppelsroeder showed that capillary analysis of an alcoholic solution of azulene yielded blue, violet, and rose colored zones. Elution of the blue zone with alcohol yielded cleaner blue dyes. Thus the technique had applications as a preparative method.

In a book published in 1904[2] Goppelsroeder discussed capillary analysis of urine samples obtained from patients at the Basel Bürgerspital where he did most of his work. In searching for compounds which might be present in the urine, Goppelsroeder developed tests for identifying these materials. A comparison of his tests with those in use today is tabulated below:

Compound	Goppelsroeder's test	Present test
Arabinose	Fehling's solution	Aniline oxalate
Taurocholic acid	Furfural—H_2SO_4	$SbCl_3$
Leucine	Quinone powder—NaOH	Ninhydrin
Urea	$CuSO_4$—NaOH	Hypochlorite
Creatine	Alk. picric acid	Alk. picric acid
Uric acid	$AgNO_3$	$Hg(NO_3)_2$

To test the strips a section was cut out for the color reaction and rematched for possible elution and re-analysis.

Although he recognized the possibility of using aqueous solvents, his work usually entailed the use of pure liquids or aqueous solutions. Goppelsroeder did not have the concept of R_f but always recorded the height of rise of solvent and of the colored zone. He tried to relate these distances to the concentrations of materials being studied. With smaller quantities of compound and with greater sophistication in choice of solvent he might have obtained discrete spots rather than zones.

In another work published in 1901[3] Goppelsroeder reviewed the history of capillary analysis and detailed his own work between 1861 and 1901. He used wood, wool, linen, silk, and parchment as well as filter paper in his experiments. He also used filter paper impregnated with albumin and suggested conversion of the cellulose to oxycellulose to give greater definition.

During his career Goppelsroeder investigated dyes, alkaloids, fats, and oils, petroleum products, beverages, and inorganic ions. In his later dye experiments he attempted separation of mixtures containing as many as ten components.

In his work with natural oils, Goppelsroeder studied the rise of pure oils over periods as long as thirty days. The height of rise was characteristic for each oil and the results were reproducible.

Little of Goppelsroeder's work is of immediate value today, but many of his innovations such as elution and re-analysis, impregnation of paper, and use of adsorption media other than paper are being applied and rediscovered.

(I am indebted to Dr. Max Feurer for supplying the few biographical facts presented above.)

[1] GOPPELSROEDER, F., *Verhandl. naturforsch. Ges. Basel*, part 3, 268 (1863).

[2] GOPPELSROEDER, F., "Studien uber die Anwendung der Capillaranalyse," E. Birkhaüser, Basel, 1904.

[3] GOPPELSROEDER, F., *Verhandl. naturforsch. Ges. Basel*, 14, 1–545 (1901).

Proceedings of the

Pacific Southwest Association of Chemistry Teachers

Design of a Chemistry Lecture Room

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In view of the increasing complexity of modern college chemistry buildings, it is perhaps not surprising to hear considerable criticism of the architects who have designed these structures. Frankly, no one professional such as a general architect should be expected to cover in expert fashion so many complex arts as are now involved in these technical projects. With like frankness, one must also admit that the faculties and administrations of the colleges concerned share a substantial part of the blame for the numerous mistakes that have turned up. After all, the architect has to get along with his job. Unless he can get prompt, continuous, and carefully-considered advice from a competent faculty building committee, we can be sure that plenty of errors will be made.

The general lecture room is no exception to the above comment of warning. With acoustics, illumination, and visual education involving new complexities, the committee should not leave the lecture-room problem solely in the hands of a general architect without early and detailed study on their part.

Lecture-Room Problem First

For the purposes of this particular discussion a room in the range of 200 to 350 seats is assumed. First of agenda at the conference table of landscape architect, building architect, and building committee may well be the location and landscape level of this room. Establishment of floor levels, especially in the case of sloping terrain, would be one of the first topics. Possibility of exterior entrances and exits would be important, particularly in mild climates where traffic does not have to be confined to indoor passageways.

Slope of the main auditorium floor must now be decided. Usually the choice lies in a range between a small angle of declivity, with rear seats about one half story above the speaker's level, and the steep design, with front and rear just one story apart; that is, a 12- to 14-foot differential. In the illustrations (Fig. 1 and 2) the differential chosen by the staff was slightly over one half story.

Principal argument for the smaller slope comes from those who use alternate seats in the hall for examinations, and who claim that it is much easier to prevent copying of material from papers of students in front. Somewhat more emphatic a case may be made for the steeper slope, in view of greater ease of observing lecture demonstrations, and better acoustics. Ease of observation is matched by more efficient passage of direct sound waves from lecturer to auditor, with minimum sound interference from heads of auditors in front. It may also be easier for the architect to provide auditor access, plus required emergency exits, when exactly one story intervenes.

In wing-style buildings, as contrasted with the hollow-block model, the lecture hall may well be adjacent to an exterior public court, with at least rain shelter nearby; or at the outer end of a short protruding wing. The back of the auditorium (main entrance) should be at the outer end, permitting crowds to enter and leave without encumbering corridors. Demonstration desk and preparation room may then be near to a storeroom.

This plan immediately calls attention to optional locations when the terrain slopes appreciably. Other factors permitting, the floor at rear-seat level may well be only a few inches above ground level outside. This simplifies the use of the hall by wheel-chair patrons, who should have easy ramp access. Such arrangement at once sets the plan of floor levels. According to slope chosen, the instructor's position in the lecture room will then be from 7 to 13 feet below entrance level. This position should be in phase with one of the regular floors, to facilitate movement of heavy apparatus from elevator to demonstration desk. The choice between gradual and steep slope may also be guided in part by the fact that the projection lantern should be at about the same level as the center of the screen. See discussion of projection positions in a later column.

If urban plot restrictions render the (undesirable!) hollow-block building design necessary, a lecture hall may sometimes be located advantageously as a bridge across the center of an otherwise open rectangular court. The one-story differential, rear to front, then becomes practically mandatory.

Early Acoustic Advice

Shape, and to a limited extent even size, of the hall should now be set by a competent acoustic engineer. Since efficient modern ventilation is assumed in this discussion, cubic capacity should be minimum for the number of auditors to be housed; about 125 cubic feet per seat is recommended from the acoustic standpoint.

Unfortunately some auditoriums, even of recent construction, have been designed without attention to acoustics beyond the use of whatever amount of "acoustic" wall covering was thought to be adequate to eliminate reverberation of sound. The acoustic engineer, if any, gets to the job too late to advise on basic design. Such basic design, involving shape of room, considers

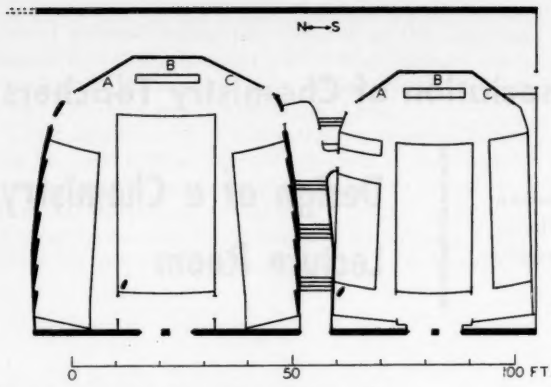

Figure 1. Floor plan of two adjacent lecture rooms.

primarily the problem of delivering adequate sound energy, without distortion or extraneous noise, to the ears of the student auditor, in the back as well as the front of the room.

As an illustration of a number of details in efficient acoustic design, the plan and section of two adjoining lecture rooms are sketched herewith in Figures 1 and 2. This design is approximately as originally suggested by V. O. Knudsen and L. P. Delsasso, and adopted with slight modifications in the Chemistry Building, U.C.-L.A., by University Architect C. C. McElvy and executive architects Stanton and Stockwell of Los Angeles. The longitudinal section (Fig. 2) applies to the larger hall. Very slight modifications have been made in these sketches, based on experience with the actual rooms as built at Los Angeles. These halls, capacity 352 and 234 auditors in regular seats, plus 6 or more wheel-chair patrons in each room, have in general given excellent service, along with an adjoining duplicate of 234 capacity used by another department. Each of these rooms presents the following features:

The conventional two front corners, normally to the right and left of the lecturer's stand, are eliminated as worse than useless from either acoustic or visual standpoint. Corner space thus excluded is relegated to the back area where it is convenient for other purposes, including demonstration-equipment storage. The resulting polygonal wall front effects a substantial reinforcement of sound, and also permits maximum visibility of the long 3-section chalkboard used by the lecturer. Care is taken not to have any long stretch of curved rear wall, to avoid the sound-focusing effect which would come from a large concave surface back of the rear seats. The ceiling is "staggered" (Fig. 2) with angles carefully chosen to deliver reflected sound to the center and rear sections, where increased energy is most needed. Such detoured sound waves are still not focused on one point or line.

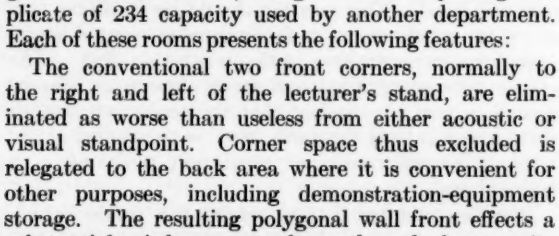

Figure 2. Vertical longitudinal section of north lecture hall of Figure 1.

Side walls in these rooms are either slanted or broken into sections, zigzag fashion. Such design has the desired directive effect for reflected sound, and is used to prevent "flutter echo" which normally occurs between widely-spaced parallel side walls. Flutter echo, a form of rapid pulsation, is an unpleasant nuisance that tends to obscure auditors' distinction between similar consonant sounds, e.g., *f* and *th*.

If objection be raised to such irregular wall designs, either from cost or architectural problems just outside of these walls, and parallel walls are actually used, one must then spend some extra money on increased acoustic side-wall covering. The 40% coverage, cited below, may have to be boosted to a value near 100%. This will stop the flutter, but will result in permanent loss of sound intensity in rear-seat sections. In the end there may be no economy.

In all of this acoustic design, it is highly recommended that the detoured journey of a sound impulse, speaker-to-wall-to-auditor, be not delayed much more than $^1/_{50}$ second in comparison with the direct impulse, speaker to auditor, which did not detour. In other words, the indirect path should be not much more than 20 feet longer than the direct. In very small halls, housing less than 100 persons, this problem becomes so unimportant, and the reinforcement of sound so unnecessary, that a simple acoustic treatment of ceiling and walls, or of ceiling alone, suffices.

Treatment of Ceilings and Walls

For any but the smallest lecture rooms, no sound absorbent whatsoever should be placed on ceiling or front walls. Here is found one of the most widespread errors in lecture-room architecture, even in some very recent construction, where perforated tile or "acoustic plaster" is placed on a ceiling. On the rear wall, however, complete coverage, with the best absorbent suitable to the job, should be provided. Side walls may be as much as 40% treated in a random pattern of tile sections, provided the problem of flutter echo has been properly disposed of in the first design.

The choice of acoustic covering depends on the degree of architectural elegance established for the building—something beyond the scope of this article. If the new chemistry building is to be regarded strictly as a plain workshop, then the common but very efficient fiberboard acoustic tile will suffice. Such tile with *random* layout of perforations is somewhat more artistic than the more dreary sieve-like pattern. In the Los Angeles lecture rooms (Fig. 1) perforated ornamental plywood panels resting on fiberglass batts give the same acoustic effect with much greater elegance of finish.

Recent developments show that thick acoustic slabs, with the perforated board layer first mounted in front of an air space and then attached to a wall, are superior to common thin tiles cemented simply to a wall. These units, at first seeming to be cumbrous, may be incorporated surprisingly well into modernistic "streamline" architecture now so popular.

Renovation of Treated Walls

Particularly in a region subject to atmospheric pollution, it is important not to use an "acoustic" wall finish which cannot be renovated by simple painting

without destruction of sound-absorbent character. In other words, never depend on acoustic plaster, cinder block, or other finely porous wall surface no matter how good the acoustic effect would be at installation time. The first repainting would fill the minute holes which are essential to sound absorption. Standard *coarsely* perforated tile or plywood, however, escapes such calamity provided the painter uses thin, finely-divided lacquer spray which will not choke or blanket the porous material at the bottom of an acoustic hole. Repeated refinishing is then feasible.

In these lecture rooms no trouble is encountered when an inexperienced lecturer attempts to speak to his audience while he stands, back to his auditors, writing on a chalkboard. The sound reflection from chalkboards and adjacent smooth walls at the side and above gives adequate audibility. But any sound that once passes the rear seats and strikes the rear wall should be as completely absorbed as possible. Its delayed return into the central audience area would interfere with the next following sounds.

Exterior Noise

With the advent of jet airplane travel, noisy British automobiles, and general campus traffic racket, perhaps this topic should have been placed first. Certainly the acoustic adviser will scrutinize the ability of a light truss roof over a lecture room to exclude aircraft noise. Thereafter will come comparison of wall materials, including the usefulness of partitions of heavy mass. If busy corridors are to flank the lecture room, "staggered studdings" may be used as an option in place of heavy tile or brick. In this design the exterior plastered wall is not directly connected, as through one studding, with an interior plaster layer.

One of the unfortunate results of modern building-cost inflation parallels the modern requirements for efficient ventilation. Says the building economist: If flues are expensive, reduce their size and increase air velocity. Result, a roaring noise. Building committees should insist that the plenum directly in front of a noisy high-speed fan be treated heavily with fiberglass or equivalent, and also that the outlying flues, approaching inlet registers in the auditorium, have like treatment. In other words, the noise comes both from machinery and from turbulent air in flues.

A common error in lecture-room design is seen in the placement of a main entrance at the front of the room. Such arrangement is a persistent nuisance during the first part of a lecture, due to distraction of student attention by entry of latecomers, who are often well dressed and chic. In the example of Figure 1 the front doors are strictly exits only, and are of course required by safety laws. Entrance is from the rear only, at ground level. If severity of winter climate or some special architectural problem makes the restriction of the front door as exit not acceptable, the instructor should still have the privilege of locking this door against entry of latecomers just at the moment he starts his class session. Exit—perhaps under emergency conditions—would of course be unrestricted. Operation of a "panic bar" allows escape in a hurry. Even if the fire department would allow it, no lecture hall should be built without a *rear* door.

Since the seats midway between side walls of a room are the best from hearing standpoint, no aisle was placed in the center. With slant projection, described later, the filling up of the center strip is of no import audio-visually. The seats are upholstered, yielding almost as good protection from reverberation when vacant as occupied. Windows are adjudged worse than useless, since they merely introduce problems of excluding both undesired sound and light.

With no posts allowable in the lecture room, either heavy and costly girders are required overhead, or a simple truss roof with no attempt to add upper stories. In Figure 1 the heavy girders were used, with a library overhead. Obviously a "dry" function, employing no water service or sewer lines, should be the only installation permitted over the lecture hall. The ceiling of the hall should not be more than 20 feet high, and ample space is available within two stories for flues and electrical equipment. Further details of lecture-hall acoustic design are given by Knudsen and Harris.[1]

If the lecture room is to be used to any extent for examinations under alternate-seating regulation, the three blocks of seats, right, center, and left, should as far as possible contain odd numbers of seats in each row.

Illumination

It would be hard to cite an example of improvement in standard of living during the past century more striking than illumination of places of public assembly. For example, one may take the intensity of illumination on hymn book or notebook, in church or classroom. With exception of the first two uncertain items, the following entries represent American recommended practice of the time; ratings in foot candles:

1860,	rural church, kerosene lamps, probably much under	1
1880,	church, fish-tail illuminating-gas lights, still under	1
1906,	church, carbon-filament incandescent lamps	1
1921,	college lecture room, mazda tungsten lamps	10
1945,	college lecture room, fluorescent lamps of early design	30
1958,	college lecture room, fluorescent lamps, improved, layout as recommended by manufacturer	50
1960,	college lecture room, forecast of the probable official recommendation of illumination engineers	100

If this seems to be running to excess, one should note current published recommendations for special services:

Illumination on surface of proofreader's desk	150
Illumination on table, factory inspection of industrial product	300

The immediate impression of all this on the layman is one of fear that the illuminators, eager to sell lamps, are in danger of causing eye strain or even serious retinal injury. The answer to this alarming question seems to be—No. The illumination engineer points out that a person reading a book outdoors *in the shade* of a building, otherwise under cloudless sky, is actually gazing at a white surface illuminated at 500, 600, or even 800 foot candles. The fear, says the engineer, is not a matter of mere foot candles, but rather of irritating glare in certain installations where high intensity has been unskillfully attempted. Eliminate glare, and the proposal of 100 foot candles for the chemistry lecture room is one of power economy rather than hygiene.

[1] KNUDSEN, V. O., AND HARRIS, C. M., "Acoustical Designing in Architecture," John Wiley & Sons, New York, 1950.

The Significance of Glare

Fundamentally, "glare" is a somewhat vague concept not pinned down to precise measurement like the volt or ampere. It refers to excessive light from a small source entering the eye, and probably being reflected there in a pattern superimposed on other more legitimate images. It thus causes distress and reduced visibility.

For the chemistry lecture room, however, glare may be given the simplified definition as light from an intense source, usually at the ceiling, which travels laterally, but at a downward angle less than 30° from the horizontal. This leads to the rule that the principal rays from a brilliant ceiling lamp should be confined to a 120° cone with apex at the lamp and base on the floor. Such illumination operation might be contrasted with the old practice of suspending an old-fashioned arc or a transparent Mazda bulb not far overhead, with resulting intense glare. Suspension of lamps in low position was just a sequel to oldtime conditions, when all lamps were inefficient. Incidentally, glare may also come from misdirected reflection by chalkboard or from a book page.

Three principal methods are now favored for prevention of glare in a lecture hall. Two of these recognize in a rough manner the 120° specification cited above. First—and of low cost in fixture manufacture—is the louver design, commonly termed "egg-crate" or "baffle," which has swept the country since World War II. It has approval of important authority. A second school of illuminators, deploring the loss of light energy in nearly horizontal directions by intervention of opaque baffles, turns such side rays downward by refraction in clear, quasi-prismatic, quasi-cylindrical pressed-glass windows. On the single basis of first cost of fixtures, such technique is of course more expensive.

Building committees should canvass carefully the counter claims of the louver and refraction supporters. Initial cost of fixture may be compensated by less waste of light, with consequent cut in number of fixtures, amount of wiring, and assertedly lower tube-replacement and electric bills.

If the louver principle be favored, one should note that there is after all no sharp line of distinction between the extreme of a fine-mesh "egg-crate," and a simple open inverted-trough fixture, running crosswise in the room, and equipped with overhanging metal aprons fore and aft. A compromise layout of very few baffles, running across the trough, and lengthwise of the room, is then possible on a low budget for fixtures.

In the third scheme of glare prevention, both louver and refraction designs are sidestepped without specific attention to the 120° rule. This may be called the "diffusion" plan. Open fluorescent-lamp fixtures of simple design are merely countersunk up into a furred ceiling, and completely covered with flat or fluted sheets of translucent plastic. These large horizontal plastic windows are flush or nearly flush with the ceiling and are at sufficient distance from the fluorescent tubes to avoid bright lines or spots on the plastic surface. Obviously the diffusing window reduces illumination efficiency, again raising the arguments over cost of the more efficient refracting window. In the face of present rapid progress in engineering research in this field, no positive single recommendation is ventured here.

Whatever the fixture scheme may be, the switch controls should be remote, and not too many. In a lecture hall there is always the possibility of need for general lighting control in at least four positions—rear door, front door, lecture table, and a mid-position suitable for opaque projection and small 35-mm outfits. It is not practical to wire the whole power load to all of these scattered positions. One therefore uses low-voltage control circuits, and solenoid-operated switches in the main lighting circuits.

Illumination and Picture Projection

The recent extensive development of border sciences in which mathematics, or perhaps dynamic structural formulation, is worked out simultaneously with display of picture, table, or graph, makes it essential that a lecturer be able to write uninterruptedly on the chalkboard as his slides are shown, without necessity of periodic tinkering with general room lights. Such fundamental fields as physical-organic chemistry, reaction kinetics, and mechanistic biochemistry are examples.

Unfortunately, conventional recommendations for "audiovisual" room equipment overlook the chalkboard-screen combination. Numerous classrooms and lecture halls are still being constructed in which all general room lights must be extinguished when slides are shown. The lecturer must call alternately for "Lights please!" and "Lights out" as he attempts to supplement his picture projection with chalkboard work. In such obsolete performance he is compelled to inflict eye distress from alternate spells of bright light and darkness, and is cramped in his own lecture style.

In Figure 2 is seen the shielded illumination of the entire chalkboard by two rows of fluorescent lamps, which run the length of the three-section board. This particular arrangement is sketched from the excellent layout in the new chemistry building at Purdue University. The double row makes it improbable that both lamps along any one fixture unit would both fail at the same time.

It is not necessary—rather it is highly undesirable—to place chalkboard lights two or three feet out from the chalkboard surface. Such frontal displacement would throw intolerable stray light on the projection screen, and is also likely to distress the lecturer by acting as a glaring searchlight in his face. Figure 2 shows the close setting of the lights, which in practice has proved to be entirely acceptable, in spite of the greater intensity at the top of the board than at bottom.

An interesting modification of the chalkboard illumination system uses special ultraviolet ("black light") tubular lamps set in fluorescent-type fixtures. The lecturer uses fluorescent chalk. Both fixtures, lamps, and special chalk are now being featured commercially. This system, while a bit fancy, would be particularly interesting when very dark slides are being shown simultaneously with chalkboard work; for example, certain dark color slides.

Simultaneous chalkboard-screen illumination calls for two more simultaneous services. The lecturer

himself should have either a very carefully shielded desk lamp, or a spotlight overhead giving him about 10 foot candles on his notes; the former is probably better. The student audience, using tablet chair arms, should have about two foot candles from carefully designed and placed ceiling spotlights. More than the two foot candles illumination is questionable, due to the widespread student habit, in well-heated American buildings, of appearing coatless in white shirts or blouses. Excessive stray light, reflected from so many white garments, interferes with color slides. If the committee insists on more downlights, they should be wired alternately in two circuits. The architect should not attempt to cover the area with a small number of large downlights, which would have too wide a light pattern and again interfere with color projection. Like the main light controls, these downlights should be handled at any of the various control positions by inexpensive electromagnetic switches.

Slanting Projection

With the movie theater as a standard, it is conventionally presumed that the projection screen should be in the center, as at *B* in Figure 1. In the Los Angeles chemistry halls, however, with design in close agreement with Figure 1, it was discovered incidentally, several years ago, that the side position *C* is preferable. Advantages of the slant arrangement much outweigh the trifling disadvantage coming from slightly reduced visibility in the southeast corner of the room. Even this disadvantage applies with appreciable significance only to a few seats in the south room.

In the slant arrangement, in regular use at Los Angeles with approval of both local and visiting scholars, the lecturer may view his notes, see the audience, the slide projection, his chalkboard writings, and even the pointer on the desk in front of him, all without having to take even one step aside. The projector sends its beam from a position in or near the northwest corner of the room obliquely across the central block of seats.

The special position of the two Los Angeles halls, backing up to a public court, makes the development of good projection rooms difficult. In other projects the architect may readily provide such rooms specially for slant projection, or for both slant and center service.

A modern wide periodic chart, with representations of actinides and lanthanides, may well appear over chalkboard *B*. An oxidation-reduction-potential chart could be over *A* or *C*. It is assumed that the old-fashioned atomic-weight chart, in addition to a periodic table, is now considered superfluous. If one chalkboard section is desired in double, motor-driven system, let that be section *A*. Simultaneous chalkboard and screen display, in a darkened room, would then be confined to *B* and *C*, *A* being unilluminated.

Projection Screen and Objective

Warning is given not to leave the prescription of screen and objective sizes to lantern sales personnel. These commercial representatives often assume that all slides are properly masked, and specify too short a focal length of lantern objective. Unfortunately many visiting scholars pay no attention to masking, and will bring slides with picture sections as wide as 90 mm, instead of the 75-mm commercial maximum for the $3^1/_4$-in. × 4-in. slide. To be realistic, the building committee should provide lantern, objective, and screen of proper proportions to project a 90-mm slide image within the horizontal limits of the screen. For example, a lecture hall in which the distance from rear seat to screen is 45 feet should have a screen on which the approved 75-mm slide image would be magnified to a size not less than $^1/_6$ of 45, or $7^1/_2$ feet. With allowance of 20% for oversize (90-mm) slides, a standard 9-foot screen would then be the minimum requirement.

In addition to the 20% allowance, the screen should have an extra allowance at the top of 3 feet in vertical length, to insure against ripping of cloth from roller by a careless attendant who may forget that a screen in this hall has a normal position *above* the chalkboard.

If the popular 35-mm slides are to be projected from such distance as 45 to 50 feet, one should avoid the common optical error of saying "small slides, therefore small objective." Dependence should not be placed on high-wattage projection lamps, which are very hot. Other factors being equal, illumination on the screen falls with increase of projection distance, though not in simple linear proportion.

PSACT Summer Conference on the Teaching of Chemistry

Location: Beautiful Asilomar, a rustic park on the ocean front of the Monterey peninsula, California.

Dates: August 17–August 21, 1959.

Invited participants: Chemistry teachers and their families from all locations.

Program: Lectures by authorities in various fields of chemistry, demonstrations, discussions of curriculum problems, evening illustrated lectures on topics of international interest, and trips to nearby points of interest.

Cost: $8.50–$10.50 per person per day for meals and lodging.

For information, write: Sister Agnes Ann Green, President of PSACT, Chairman and Director of the Summer Conference, Immaculate Heart College, Los Angeles, California.

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Radioactivity Experiments for High Schools Using Orange Glazed Ceramics

The discovery of radioactivity by the French physicist, Henri Antoine Becquerel, has been described by John H. Wolfenden of Dartmouth College[1] as an example in science of serendipity. If it had not rained in Paris during the last week of February, 1896, this property possessed by some elements might not have been observed for several years. Becquerel was studying the fluorescence of certain minerals after exposure to sunlight. He prepared some samples of uranium salts which he planned to expose to the sun and then to place on a photographic plate wrapped in black paper. Since the sun shone only intermittently on Febuary 26 and 27, he placed the salts and the plates in a drawer. On March 1, for some obscure reason, he developed the photographic plates without exposing the samples to the sun, and yet found dark images of his samples. Becquerel continued his experiments and found the fogging was the same whether he exposed his crystals of uranium salts to the bright sunlight or kept them in the dark. The spontaneous emission of radiations that he thus discovered was named *radioactivity* by Pierre and Marie Sklodovska Curie in 1898.

Before 1942, when uranium ore had little value, the ceramic industry used sodium and ammonium diuranates to produce an orange-colored glaze. Laurence S. Foster suggested that the orange glazed pottery, called *Fiesta-Ware*, be used as a source of radiation for classroom demonstrations.[2] For fifteen years all uranium supplies were stopped because of the greater value in the atomic energy program. In 1958, the United States Atomic Energy Commission released *depleted* (after removal of U^{238}) uranium once more, so we may expect to see these orange glazed dishes reappear.

Our chemistry students were asked to bring to class pieces of the bright orange-colored pottery to be tested for radioactivity with a G-M counter. Church fairs, rummage sales, attics, and cellars were the sources of the dishes. Some were contributed for the project; for others the prices ranged from ten cents to a dollar. Student projects and experiments, based on these convenient radioactive sources, were designed to accomplish the following purposes: (1) to determine the effects of radioactive dishes on X-ray film; (2) to determine the relative activity of the dishes by measuring the intensity of light transmitted through exposed spots on the film; (3) to determine the relative activity of the dishes with a G-M counter and to correlate these results with the density of exposed X-ray films; (4) to compare the activity of radium watch dial numerals and the uranium-containing glazes; (5) to compare the ability of different metals to attenuate the emitted radiations; and (6) to compare the activity of various uranium- and thorium-containing minerals.

All the experiments reported here to accomplish these objectives were developed and refined with the active participation of high school students at the Natick High School.

Preparation of Autoradiographs

Exposure of Films. Kodak X-ray Medical Film Blue Brand was used and developed in Kodak X-ray developer and fixer. Kodak No-Screen Medical X-ray Film can also be used. These may be purchased at local medical supply houses.

Samples of uranium and thorium minerals were left exposed on the film for 72 hours. The minerals were separated into rows by strips of sheet lead.

An uncovered radium watch dial was allowed to expose the film for 6 minutes and for 12 minutes. To show the scattering effects of the glass watch crystals and of the necessity of having close contact between the dial and the film, the experiments were repeated with the watch crystals replaced.

One of the orange glazed dishes was left on the film for 24, 48, and 72 hours.

Different metals (copper, lead, zinc, and aluminum) were cut into different shapes and placed in close contact with the film. An orange glazed dish was inverted over the metals to serve as a more or less uniform radioactive source for 72 hours. (See Fig. 1.) Strips of metal of nearly equal thicknesses (copper, zinc, brass, magnesium, nickel, tin, aluminum, titanium, lead, iron, and chrome-plated iron) were placed on the film, similarly exposed.

To compare the relative activity of the dishes, either two dishes

Figure 1. Autoradiograph produced by using an orange glazed dish as a source; also, showing attenuation by use of a lead dog, a copper circle, a zinc triangle and an aluminum hexagon.
Figure 2. Autoradiographs produced by orange glazed dishes, showing that some are more radioactive than others.

Presented at the 20th NEACT Summer Conference, University of Rhode Island, Kingston, August 22, 1958.

[1] "The Role of Chance in Chemical Discovery," 287th NEACT Meeting, Keene Teachers College, Keene, New Hampshire, October 13, 1956.

[2] FOSTER, L. S., "Demonstrating Radioactivity by Autoradiography," J. CHEM. EDUC., **27**, 225 (1950).

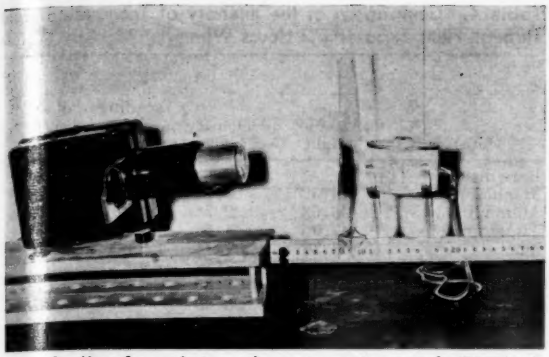

Figure 3. Use of a projector and exposure meter as a densitometer to measure blackening of films.

or four were placed on a sheet of film and exposed for 72 hours. (See Fig. 2.)

Development of Films. The films were developed in Kodak X-ray developer for 2 minutes, under a red light; fixed for 5 minutes in Kodak X-ray fixer; and washed in running water for 30 minutes.

After developing the films, the blackening can be used to estimate the relative radioactivity of the sources. The light transmission procedure, used to measure the degree of exposure, is described in the following experiment.

Determination of Light Transmitted Through Exposed Areas of Films

A 100-watt, 35-mm projector was used as the source of light, as shown in Figure 3. Black paper with a small hole was placed in the slide carrier. A 3-in. focal-length lens was attached to the outside of the regular lens by means of adhesive tape. Two pieces of cardboard, 10 in. by 12 in. and hinged, were used as a film holder. Small matching holes were made in each sheet to permit the passage of light. The intensity of transmitted light was determined by means of a Weston Master Universal Exposure Meter. Various exposed areas on each film, held between the cardboards and positioned by hand at the focal point of the lens, were examined, and the readings of the exposure meter were recorded in foot-candles.

Measurement of Radioactivity

A sheet of lead, 12 in. by 18 in., was erected in front of a Tracerlab, Inc., Radioactivity Demonstrator, that has a count-rate meter scale reading *counts per minute*. The lead sheet was cut to make a rectangular opening, $3^3/_4$ in. by $^3/_4$ in. to shield all but a small portion of the sample. The intensity of the combined beta and gamma radiation of the various sources was determined using reproducible geometry. The rectangular opening in the lead shield insured that comparable areas of the samples were always presented to the meter. With the opening directly opposite the G-M tube, the lead sheet was situated at convenient distances from it: (1, 7.5, or 12.5 cm). The sample dish was held directly behind the lead shielding and the readings of the meter at these three distances were recorded. Both the front of the sample and the reverse side were measured. The window of the G-M tube was left open so that both beta particles and gamma rays were counted together (Fig. 4).

Held behind the large lead sheet, against the rectangular opening, at a distance of 1 cm from the G-M tube, the dishes showed variations in meter reading from 1800 to 2500 counts per minute (the highest value that could be read on the meter). The radioactivity of the several mineral samples is given in Table 1. Further experiments for students, utilizing minerals to produce autoradiographs, have been recommended by Professor William S. Huber of the Rhode Island School of Design.[3]

Comparison of Film Darkening with Radioactivity of Sample. After developing the films, the darkening can be used to estimate the extent of exposure to radiation. The radioactivity of the samples can also be measured. A comparison of the results is given in Tables 2 and 3.

Table 1. Radioactivity of Mineral Specimens[a]

Mineral	Location of deposit	Reading on demonstrator meter counts/minute
1. Autunite on granite	Montebras, France	250
2. Carnotite in sandstone	Black Hills, S.D.	1700
3. Cryotolite	Bancroft, Canada	350
4. Ellsworthite	Hybla, Canada	1100
5. Euxenite	Voandelaka, Madagascar	>2500
6. Fergusonite	Madawaska, Canada	1900
7. Gumite with uraninite	Grafton Center, N. H.	>2500
8. Monazite	Raada, Norway	1700
9. Monazite sand	Travancore, India	600
10. Priorite	Iveland, Norway	1700
11. Samarskite	Mitchell Co., N. C.	>2500
12. Thorianite	Andolobe, Madagascar	2000
13. Betafite	Gunnison Co., Col.	2500
14. Torbernite	Cornwall, England	1750
15. Uraninite (pitchblende)	Lake Athabaska, Can.	>2500
16. Uraninite	Spruce Pine, N. C.	>2500

[a] Procured from Ward's Natural Science Establishment.

Figure 4. Measuring the radioactivity of orange glazed dishes held behind a rectangular hole in a lead sheet to give constant "geometry."

Table 2. Comparison of the Intensity of Light Transmitted Through the Film and the Duration of Exposure

Exposure duration (hours)	Light-meter readings (foot candles)
24	13
48	5
72	4

Table 3. Comparison of Film Density After 72 Hours Exposure with Radioactivity of Sample

Light transmittance (foot candles)	G-M Meter reading (c/m at 1 cm)
3.2	2300
3.6	2500
3.6	2200
4.0	2100
4.5	2050
10.0	1950

[3] HUBER, W. S., "Autoradiography as a Science Project," J. CHEM. EDUC., **28**, 226 (1951).

Attenuation of Radiations by Metals. A comparison was made of the shielding effects of various metals placed between a selected dish, used as a radiation source, and one piece of film. The results, recorded in Table 4, show that in general the intensity of the transmitted light rose as the density of the metal rose, rather than with the atomic weight. Part of the fluctuation is caused by the variability of thickness of the metal strips, which could not readily be procured in identical thicknesses. On the other hand, the measured radioactivity fell as the shield became more dense. Titanium is especially interesting because its density is only about six-tenths that of iron while its atomic weight is eight-tenths. It is a much poorer shield because of the lower density.

Table 4. Comparison of the Intensity of Transmitted Light Through Films Exposed 72 Hours When Shielded by Metals

Metal	Atomic weight	Density (g/cc)	Light meter readings (foot candles)	Reading of G-M meter (c/m)
Bare dish	...	...	0.8	220
Magnesium	24.32	1.74	6	70
Aluminum	26.98	2.7	8	45
Titanium	47.90	4.5	9	40
Zinc	65.38	7.14	14	75
Tin	118.70	7.28	14	100
Iron	55.85	7.86	14	50
Brass (yellow)	...	8.40	14	75
Nickel	58.71	8.90	13	125
Copper	63.54	8.92	14	100
Chrome-plated iron	...	...	14	50
Lead	207.2	11.34	17	0
Developed unexposed film	...	...	18	...

The question always arises as to whether these radioactive dishes constitute a health hazard. U^{238} decays to Th^{234} (UX_1) with the emission of an alpha particle, with a half life of 4.49×10^9 years. Obviously uranium is only very weakly radioactive, and the alpha particle cannot escape from the glaze. Th^{234} decays with a half life of 24.1 days, emitting low energy beta particles and gamma rays, to form Pa^{234} (UX_2). This granddaughter is the chief source of the radioactivity of natural uranium. It has a half life of 1.175 minutes and decays emitting energetic beta particles (2.3 Mev) and gamma rays, to form U^{234} (U-II) which has a long half life, 2.5×10^5 years. Samples of pure U^{238} will contain these daughter products in equilibrium after a period of six months. As a result of the UX_2 activity, relatively high surface dose activities can be measured with suitable equipment. The following dose rates are cited in USAEC report No. AECD 2753: pure uranium metal, 239 mrem/hr; uranyl nitrate hexahydrate, 114 mrem/hr; orange oxide (UO_3), 208 mrem/hr; and black oxide (U_3O_8), 207 mrem/hr. The accepted standard for exposure to the hands is 1500 mrem/week. The dose required to produce reddening of the skin is at least a thousand times greater. While continuous contact with orange glazed dishes for long periods of time would exceed the tolerance dose, during normal use as eating utensils, this exposure would not present a health hazard.

This series of experiments shows that, by using an inexpensive and harmless source of radioactivity, students can determine for themselves the many characteristics of radioactivity. They are able to learn some of the laboratory techniques used to measure and to characterize it and to prepare autoradiographs. This latter technique will also introduce them to the art of photography which may later become a hobby.

Chem Ed

LETTERS

To the Editor:

The liberal arts colleges should be grateful to William Caldwell for his article in the February issue of the JOURNAL OF CHEMICAL EDUCATION. One reason that liberal arts college graduates do so well in our graduate schools as teaching assistants or teaching fellows is simply that they studied where the chemistry professors do the teaching.

ANDREW A. SHEROCKMAN

WESTINGHOUSE ELECTRIC CORPORATION
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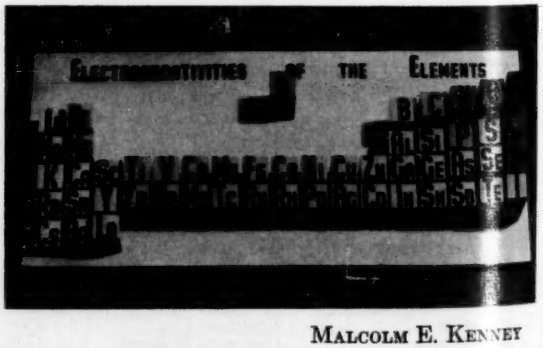
To The Editor:

The accompanying photograph shows a means of displaying the relationship between the electronegativity of an element and its position in the periodic table. (See also TOMKEIEFF, S. I., *School Sci. Rev.*, **28**, 244 (1957), and SANDERSON, R. T., J. CHEM. EDUC., **33**, 443 (1956).) The height of the block bearing the symbol of the element implies the magnitude of the electronegativity. Color coding also can be used to emphasize relative differences.



MALCOLM E. KENNEY

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Chem Ed

BOOK REVIEWS

Organic Syntheses with Isotopes. Part I

Arthur Murray, III, and *D. Lloyd Williams,* University of California, Los Alamos Scientific Laboratory. Interscience Publishers, Inc., New York, 1958. x + 1146 pp. 16 × 23.5 cm. $25.

In the preface to "Part I: Compounds of Isotopic Carbon" the authors state "there seems to be a real need for a book which comprehensively collects and describes the scattered information pertaining to isotopic synthesis." The reviewer feels that the authors have fulfilled this need magnificently. The book is much more, however, than a compilation of synthetic procedures, since important information is often given in the notes at the end of each topic pertaining to degradative procedures for, and mechanistic implications of, the work cited. Following an excellent Introduction (Chapter 1) in which are discussed the arrangement of the book, nomenclature of labeled compounds, properties and procurement of isotopes, specialized techniques, the isotope effect, radiation decomposition of labeled materials and health hazards, Chapters 2 through 14 cover: Acids, Acid Derivatives, Amines, Carbonic Acid Derivatives, Carbonyl Compounds, Ethers, Heterocyclic Compounds, Hydrocarbons, Hydroxy Compounds, Onium Compounds, Sugars and Sugar Derivatives, Steriods, and Vitamins. The Table of Contents is so subdivided that it can be used ordinarily to find a given synthesis without recourse to an index. The reviewer was impressed with the comprehensiveness of the book, which includes references not only to the open literature, but also to the many Atomic Energy Commission reports of Argonne, Brookhaven, and Oak Ridge National Laboratories, the University of California Radiation Laboratory, the Los Alamos Scientific Laboratories, and others. Further, where several syntheses for one compound exist the authors have made an attempt to evaluate the most feasible method. The reviewer agrees with the authors that: "This book should not be confined in its use to the preparation of labeled compounds alone, but it should be of considerable general interest to the organic chemist because the procedures were usually chosen for or developed to give high yields."

Any book has drawbacks and despite the fine arrangement of the Table of Contents, the absence of an index to Part I is particularly irksome, Since Part II, which will contain the index to both volumes, treats the isotopes of the halogens, hydrogen, nitrogen, oxygen, phosphorous, and sulfur, it is conceivable that some chemists will wish to own Part I and not Part II, and thus will be forced to use the book without an index. Further, although Murray and Williams appear to have developed a nomenclature for compounds of isotopic carbon which can be applied to most of the presently known carbon-labeled compounds, such names as "benzophenone- (1,1′), (1,2′), (1,3′), (1,4′), (2,2′), (2,3′), (2,4′), (3,3′), (3,4′), (4,4′) - $C^{14}_{2l}/_{0}$" (p. 676) for ring-labeled benzophenone seem to be too cumbersome for general acceptance. Also there are cases of poor printing in the book (a formula on page 144, for example). The foregoing minor criticisms, however, are trivial when compared with the many excellent qualities of the book, which appears to have a minimum of errors and inconsistencies.

In summary, Murray and Williams, who have contributed so heavily from their own laboratory to the field of isotopic syntheses, have now compiled and written an outstanding book which, in the reviewer's opinion, will serve as a fine reference for those interested in tracer chemistry, and should be owned by any chemist working with isotopic carbon.

CLAIR J. COLLINS
Oak Ridge National Laboratory
Oak Ridge, Tennessee

Semimicro Experimental Organic Chemistry

Nicholas D. Cheronis, Professor of Chemistry, Brooklyn College. John de Graff, Inc., New York, 1958. xvi + 400 pp. 16 × 24 cm. $5.50.

Based on the author's much earlier "Semimicro and Macro Organic Chemistry" (reviewed in J. CHEM. EDUC., **20**, 51 (1943)) the present work is the result of a complete rewriting. Although it is pointed out that macro procedures cannot be dispensed with, descriptions of such procedures are left to texts already available. Instead, a complete year's work involving small-scale experimentation is presented.

Covering rather more than one-quarter of the book, Part I describes both elementary and advanced techniques. Much of the apparatus used is simple and the coverage is thorough both in extent and in detail, numerous exercises being suggested. The somewhat longer Part II is concerned with the typical families of organic compounds, such as hydrocarbons, alcohols, carboxylic acids, etc. In general, the chapters are here arranged in pairs, so that descriptions of the methods of preparation and of the reactions of a given type of compound follow one another. The large number of clearly described preparations and reaction studies included in this section are alone sufficient to justify strong recommendation of this book.

Concerned with more advanced preparations and intended both for graduate and undergraduate students, Part III opens by discussing precautions in micro preparative work and the adaption of macro procedures to the small scale. As in the preceding section, the preparative descriptions are grouped systematically under such headings as Reduction and Oxidation of Organic Compounds, Alkylation by Malonic and Acetoacetic Esters, etc. Each group is concisely introduced and explained.

The two chapters comprising Part IV form a brief but systematic introduction to qualitative organic analysis, the groundwork for which is ingeniously laid in certain of the exercises given in Part II. Appendices describe suggested equipment, the care and calibration of apparatus, and the preparation of special reagents.

Reviewed in This Issue

Arthur Murray III and *D. Lloyd Williams,* Organic Syntheses with Isotopes. Part 1
Nicholas D. Cheronis, Semimicro Experimental Organic Chemistry
Walter Hückel, Theoretical Principles of Organic Chemistry. Volume 2
Francis Owen Rice, Free Radicals
John T. Edsall and *Jeffries Wyman,* Biophysical Chemistry. Volume 1
Marie Boas, Robert Boyle and Seventeenth Century Chemistry
O. A. Battista, Fundamentals of High Polymers
Willis H. Waldo, Better Report Writing
Harold P. Klug and *Robert C. Brasted,* Comprehensive Inorganic Chemistry. Volume 7: The Elements and Compounds of Group IVA
Merritt A. Rudner, Fluorocarbons
Walter D. Paist, Cellulosics
Edwin T. Williams and *R. Curtis Johnson,* Stoichiometry for Chemical Engineers
Kenneth A. Kobe and *John J. McKetta, Jr.,* Editors, Advances in Petroleum Chemistry and Refining. Volume 1

As in the case of the author's more extensive "Micro and Semimicro Methods" (reviewed in J. CHEM. EDUC., **32**, 234 (1955)), the text abounds with simple hints and tips which result only from long experience. Despite the very large amount of information, both background and experimental, contained between the covers, the text reads easily; one is inclined to forget that the subtitle is "A Laboratory Manual." It is definitely a major contribution to the teaching of experimental science.

JOHN T. STOCK
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Storrs

Theoretical Principles of Organic Chemistry. Volume 2

Walter Hückel, Professor of Pharmaceutical Chemistry, Tubinger University, Germany. Translated from the corrected 7th German edition by *F. H. Rathmann*. Elsevier Publishing Company, distributed by D. Van Nostrand Co., Inc., Princeton, N. J. xi + 1046 pp. 18 × 26 cm. $19.

It is an aphorism, commonly attributed to chemists, that, "no man can pass the same examination twice; indeed, few can pass it the first time." Professor Hückel attempts in this "Theoretische Grundlagen Der Organischen Chemie" to set forth the necessary basic concepts to enable the young student to better understand the significant guiding principles of organic chemistry and thus materially improve his performance on examinations. Moreover, those who feel that the German language is an "invention of the devil and contrary to the Scriptures" will be comforted in the knowledge that this excellent work is available in an English translation.

This volume is not a monograph; it is an intermediate text book designed for students who have had only the introductory courses in organic and physical chemistry. Inasmuch as the author critically analyzes the older concepts and traces the historical development of the subject, the young student should be completely oriented in the transition to the more modern and complex ideas.

The second volume begins with Book III, Constitution and Physical Properties. Chapter XI (58 pp.) deals with Thermal Magnitudes, as heats of combustion, thermodynamic data, density, and molecular volume.

Chapter XII (98 pp.) considers the electrical properties of molecules under the headings of: the molecule as a system of electrical charges; the dielectric constant; the determination of the dipole moment; dipole moment and constitution, symmetry, valence angle, free rotation, and intramolecular salts in aqueous solutions.

Chapter XIII (93 pp.) describes the behavior of matter in an alternating electrical field: the theory of dispersion, infrared spectra and the Raman effect, anisotropism of the polarizability, and molecular refraction.

Chapter XIV (132 pp.) explores the relations between cohesion and constitution under the following subdivisions: theorem of corresponding states, boiling points, surface tension, association, the hydrogen bridge bond, and solubility.

Chapter XV (94 pp.) examines the ordered states of organic substances in the liquid and in the crystal states then deals with lattice structures and the relations to the structure of molecules. This section concludes with an interesting study of high molecular weight polymers, principally cellulose and rubber.

Chapter XVI (52 pp.) Colloidal Chemical Properties, is an excellent treatment of the colloidal behavior of soaps, starches, cellulose, glycogen systems. The remaining chapter in Book III (150 pp.) is a thoroughgoing treatment of information relating to the chemical bond with reference to organic structures.

Book IV is a general survey of Constitution and Reaction Velocity. It contains three chapters: XVIII, Theory of Reaction Velocity (48 pp.); XIX, Reaction Velocity Constant and Constitution (133 pp.); and XX, Reaction Velocity and Equilibrium (75 pp.).

This textbook should find a generous reception among chemists; in particular, it should be useful for intermediate students seeking to develop their theoretical knowledge of classical organic chemistry.

GEORGE HOLMES RICHTER
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Free Radicals

Collected papers of *Francis Owen Rice*, Professor of Chemistry. The Catholic University of America Press, Washington, D. C., 1958. xii + 278 pp. 21.5 × 28 cm. Paper bound. $5.

Seldom can the collected scientific publications of one person be given a definitive title. The exception is "Free Radicals." Few chemists have to ask whose papers thus are being reprinted under one cover. Many of these papers are valuable far beyond any narrow field; they are important to all whose concern is the mechanism of chemical reactions. Sixty articles have been reproduced, arranged chronologically, (1931–58), but without any index.

W. F. K.

Biophysical Chemistry. Volume 1

John T. Edsall, Biological Laboratories, Harvard University, and *Jeffries Wyman*, Middle East Science Cooperation Office, UNESCO. Academic Press, Inc., New York, 1958. xv + 699 pp. Many figs. and tables. 16 × 23.5 cm. $14.

As the title indicates, this is a physical chemistry book, with coverage limited to topics which are of interest to students of biology and biological chemistry. It is also a textbook, developed out of a graduate-level course which has been given at Harvard for the past 25 years.

The topics covered include the geochemical environment and its history, the properties of water and carbon dioxide, electrostatics (including the Debye-Hückel theory, dipoles and dielectric constants, and salting-out effects) conductivity of electrolytes, acid-base equilibria (with an extended discussion of polybasic acids), and the binding of molecules by other molecules or by ions.

All of these subjects are handled with special emphasis upon their biological aspects. Illustrative examples are drawn almost entirely from systems of biological interest.

The research reputations of the authors practically guarantee the authoritativeness of the treatment, but it is satisfying to note that the selection of material for presentation is also excellent, the arrangement logical, and the exposition generally clear.

This is not to say that this is an easy book. Physical chemistry is seldom easy, and this reviewer believes that the material is sufficiently difficult to extend the better students and to leave the poor ones far behind.

It is also unlikely that the book could be used for self-study by any but the very best students. A teacher with a knack for lucid explanation should be on hand to help the students over the difficult spots and to set straight the inevitable typographical errors. The book is, however, recommended without hesitation as a text for a high-level course given by a capable teacher for capable students.

The treatment is classical throughout, with many mathematical derivations of the sort long familiar to students of physics and physical chemistry. The derivations are formal and generalized, in the best mathematical tradition, but at the same time the authors have, as they say, "considered it vitally important to give illustrations of the general principles from actual experimental data." This serves to keep the treatment down to earth and fully alive. The experimental data are beautifully chosen, and extremely up-to-date (Robbins and Boyer's work on the free energy of hydrolysis of ATP, for example).

A valuable feature of the book is the list of references, which include both up-to-date and classic monographs and books, as well as research papers. A list of problems is included at the end of the chapter on acid-base equilibria, but the teacher will have to supply his own problems on all other subjects.

The book is relatively free of misprints, but those which do occur are in some cases serious and would be quite misleading to an inexperienced student. Misstatements are even more rare. The reviewer would take exception only to the assertion that energy is required to form peptide bonds chiefly because of the separated charges on the peptide ion.

With this single exception, the material appears to be well chosen, and excellently presented. Particularly fine are the discussions of dielectric constant, *p*H standards, and the effect of imidazole on the pressure of CO_2 in equilibrium with solutions of $NaHCO_3$ (a sort of simplified hemoglobin model).

The book is heartily recommended either as a text for a course, or as reading matter for the biochemist who wishes to

(Continued on page A240)